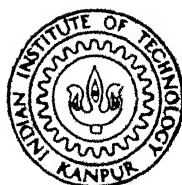# NEW NOVEL LOW-ENERGY ROUTE FOR THE PRODUCTION OF WHITE PORTLAND CEMENT

By

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INTERDISCIPLINARY PROGRAMME IN MATERIALS SCIENCE

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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NEW NOVEL LOW-ENERGY ROUTE FOR THE PRODUCTION OF WHITE PORTLAND CEMENT

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By

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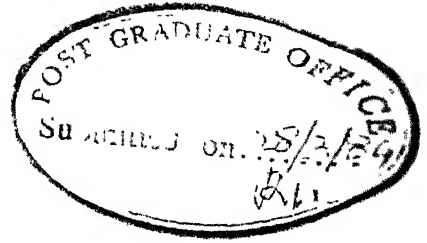
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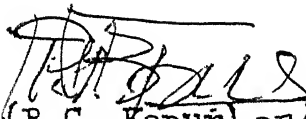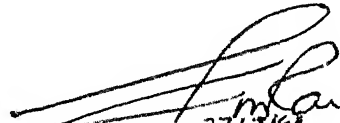
CERTIFICATE

This is to certify that this work on "New Novel
Low - Energy Route for the Production of White Portland
Cement" by D.J. Dasgupta has been carried out under our
supervision and has not been submitted elsewhere for a
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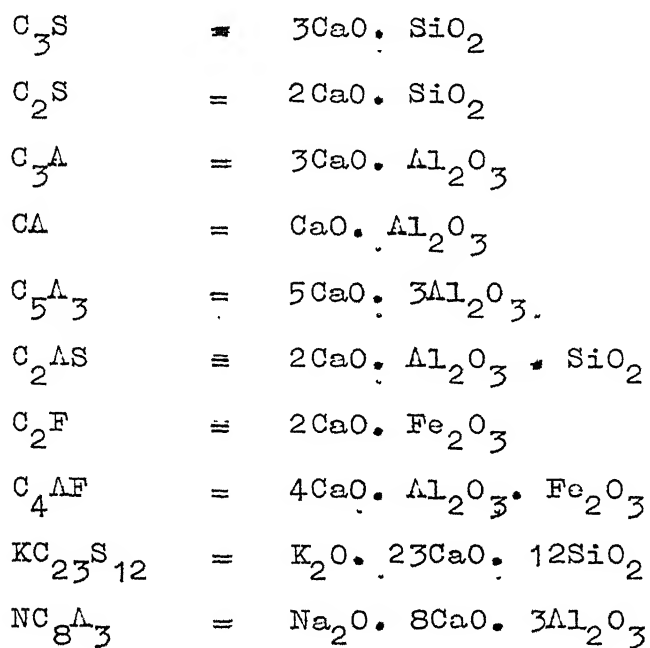
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ABBREVIATED FORMULAE

The following symbols for the cement components are used

interchangeably with the conservative notation:

$$C_3S \quad = \quad 3CaO. \ SiO_2$$

$$C_2S \quad = \quad 2CaO. \ SiO_2$$

$$C_3A \quad = \quad 3CaO. \ Al_2O_3$$

$$CA \quad = \quad CaO. \ Al_2O_3$$

$$C_5A_3 \quad = \quad 5CaO. \ 3Al_2O_3.$$

$$C_2AS \quad = \quad 2CaO. \ Al_2O_3 . \ SiO_2$$

$$C_2F \quad = \quad 2CaO. \ Fe_2O_3$$

$$C_4AF \quad = \quad 4CaO. \ Al_2O_3. \ Fe_2O_3$$

$$KC_{23}S_{12} \quad = \quad K_2O. \ 23CaO. \ 12SiO_2$$

$$NC_8A_3 \quad = \quad Na_2O. \ 8CaO. \ 3Al_2O_3$$

LIST OF FIGURES

CHAPTER - I

OBJECTIVE

1.1 INTRODUCTION:

Cements are adhesives employed to join blocks of stones, bricks etc. They bind these fragments into a solid mass when used as a grout between them. Those cements which can set and harden under water are called hydraulic cements.

Portland cement is the most common hydraulic cement. It was discovered and patented in 1824, by Joseph Aspdin, a bricklayer and mason in Leeds, England. Today about 98% of the cement produced in the world is portland cement.

Portland cement is essentially a very fine blend of calcium silicates, calcium aluminates and calcium alumino ferrites. Ordinary general purpose portland cement is gray in colour.

White portland cement is quite similar to gray portland cement, excepting for the colour and the strength. As the name suggests, the white portland cement is white in colour with a reflectance value greater than 70%. And its structural strength is about 90% of that for gray ordinary portland cement. With the addition of pigments, it can produce very light shades of pleasing pastels.

When used as a plaster, white portland cement needs no veneer or decorative treatment. No repainting is necessary either. In some areas rainfall will keep it clean. Otherwise a wash job will make it shine like new. It is essential for

fixing white or coloured sanitary wards, for making mossaic floor, or for grouting ceramic tiles and marble slabs. It is used for architectural concrete work, with certain coloured aggregates, where brilliance is desired, or for projects like road-markers, zebra-markers, lane-markers etc, where light reflectance is important.

White portland cement is a high value and a high premium loaded item. Today it costs a consumer Rs.275/- per bag of 50 Kgs., as against Rs. 75/- for the same amount of gray portland cement. Besides it is not easily available in the market. As per todays market position, a consumer has to pay the full amount in advance and then wait for 4 weeks atleast before he gets the delivery.

The high cost of white portland cement is justified to a certain extent by the exacting nature of manufacture, which requires some 80 separate and continuous operations; the use of a great deal of heavy machinery and equipment; and large amount of heat and energy. The capital investment per worker is among the highest in all industries.

The process of manufacture has to ensure that there is no contamination of Fe_2O_3, TiO_2, Mn_2O_3 in the raw materials as these impart colour. Highly pure and a high grade limestone and argillaceous aggregates are essential. The high grade limestone requires a great power for grinding. Then special precautions have to be taken in order to prevent the iron contamination during the manufacture, specially from the

kiln refractories and from the grinding media. Slightly reducing condition during the burning and rapid quenching of the clinker, tends to keep the Fe in the ferrous state in solid solution of C_4AF, thereby avoiding the intense colouration imparted by the ferric ions. But loss of Fe in the raw material means the loss of the most important fluxing agent. This raises the firing temperature and hence the energy cost.

The energy requirement in crushing of lime stones, grinding of raw materials, grinding of the clinker, clinker formation etc., forms the bulk of po land cement manufacturing expense. The net theoretical heat required to form 1kg. of ordinary gray clinker from 1.55 kgs. of dry Ca CO_3 and clay after grinding is 420 K cal. It can be seen from the following tables:

TABLE # 1.1

HEAT ABSORBED	Kcals./Kg.
1. Heating raw materials from 20° to 450°C	170
2. Dehydration of clay at 450°C	40
3. Heating materials from 450° to 900°C	195
4. Dissociation of $CaCO_3$ at 900°C	475
5. Heating de-carbonated materials from 900° to 1400°C.	125
6. Net heat of melting	25
	1030

TABLE # 1.2

HEAT EVOLVED

		KCals./Kg.
1.	Exothermic crystallization of dehydrated clay	10
2.	Exothermic heat of formation of cement compounds	100
3.	Cooling clinker from 1400° to 20°C	360
4.	Cooling CO_2 from 900° to 20°C.	120
5.	Cooling steam from 450° to 20°C including condensation to water.	20
		610

Net theoretical heat required to form 1Kg.
clinker = 1030 - 610 = 420 Kcals.

For different raw mixes, and for slightly different data this net theoretical value ranges from 400 to 430 Kcals/Kg. of clinker. The net heat of melting arises from the failure of all the glass to crystallize on cooling and is obviously a variable factor. The value to be used for the exothermic heat of crystallization of the dehydrated clay at about 900°C is also variable and may be greater by about one-half than that used. The above data is based on kaolinite alone.

The heat required in practice however, is considerably greater than the theoretical value, on account of the heat lost in the exit gases, in the clinker discharged from the cooler, in radiative and convective losses from the kiln, and in evaporation of water from the slurry. With a modern

wet process kiln thermal efficiencies are no much above 30% and so it actual practice the heat required to form I Kg. clinker would be around 1400 Kcals. Detailed discussion is given in section # 2.12. However considering a modern semi dry or dry shaft kiln process with special heat recuperators the thermal efficiency value may approach 50%. Even then the actual heat required to form 1 Kg. clinker from $CaCO_3$ and clay would be around 840 Kcals. atleast.

Apart from clinkerization, energy is consume in other stages also. The stages which are followed in most of the white portland cement production units are given below:

1. Purification of argillaceous raw materials using floatation techniques, in order to remove colour imparting compounds like Fe_2O_3, TiO_2 and Mn_2O_3.

2. Crushing of high grade calcareous raw materials requiring great grinding power.

3. Grinding of proportioned raw materials.

4. Grinding of clinkers.

5. Handling and movement of materials.

The above discussions therefore indicate the necessity of developing a new cost effective low energy route for the production of white portland cement through a proper selection of raw materials.

1.2   HOW IT IS PROPOSED TO FIND A LOW ENERGY ROUTE:

By selecting an argillaceous raw material like rice husk ash which hardly contains any Fe_2O_3, Mn_2O_3 and TiO_2, we can avoid the first step of production. Rice husk ash is about 95% pure silica.

By selecting slaked lime as the source of calcareous material we avoid the second step of production. Slaked lime, which is produced as a by-product in an Acetylene plant, is an ideal source of calcareous material. Besides being very pure it is very cheap. Being in the colloided suspension form, when in water, it settles down in an approximately 5 micron particles size. But then from each kg. of slaked lime, 0.243 kg. of water will have to be driven out.

As already shown in table # 1.1 and 1.2, 1Kg. of ordinary gray clinker formation from 1.55 kgs. dry calcium carbonate and clay consumes at least 840 to 1400 Kcals. of heat during the burning operation. Energy required for clinker formation of white portland cement is even higher. Using rice husk ash we can save on the large amount of heat required for dehydration of clay. Clay dehydrates at around 450°C requiring 112 Kcals./kg. of heat as determined by Tschernobaeff.(1). However, Mellor and Holdcroft reported (2) a value of only 41.9 Kcals/kg. Besides endothermic decomposition of Kaolin takes place near 500°C corresponding with the formation of free SiC_2, Al_2O_3 and H_2O. This too can be avoided using rice husk ash which have been fired at low temperature and hence

which is amorphous in nature. Rice husk ash does not contain alumina.

Again the heat requirement during the burning operation can be further reduced by achieving the reactions at a lower temperature. This would however mean a lower rate of diffusion and hence a lower kinetic rate and a longer duration of firing. But then, from the fuel economy point of view, at around 1200 to 1300°C, for each 23°C lowering of temperature one can burn the same fuel for 1 hour more. Again low temperature clinkerization would mean lower radiative loses which is proporational to the fourth power of temperature. Low temperature drastically changes the furnace design, reducing the cost of furnace brick . Even the maintainence cost will go down due to less harsh thermal degradation. Lower investment and lower maintainence cost mean lower cost of production.

The low temperature reactions can be achieved using highly reactive raw materials. Slaked lime is around 5 micron in size. About 48% to 49% of unground rice husk ash is -100 mesh ASTM size. Besides ash is exceedingly friable. Once ground for 10 minutes in mortar and pestle, it becomes well below -200 mesh ASTM size. Because of very fine size and hence large specific surface area, the kinetics is vastly improved. For details refer to section 2.13. A judicious choice of low melting fluxes would provide the liquid phase diffusion leading to faster transportation of the reacting species.

About 80 K.W.H. of electrical energy is required for grinding each ton of clinker. Through appropriate phase transformations, if changes in specific volume can be effected during the cooling process and if less of glassy phase can be formed, one can end up with a friable clikner. This will lower the cost of the last stage of production.

1.3   OBJECTIVE OF THIS STUDY:

It is proposed to make friable white portland cement at the lowest possible temperature-time schedule using following primary raw materials.

1. Ground rice husk ash.

2. Slaked dry calcium hydroxide.

3. Actified bayer's alumina.

This involves the production and characterization of white rice husk ash and slaked lime.

For facilitating the clinkerization the following fluxes are proposed to be used:

1.   2% Magnesium Oxide by weight.

2.   5% Magnesium Oxide by weight.

3.   2% Boric acid by weight.

4.   2% Calcium Fluoride by weight.

5   2% Calcium Phpsphate by weight.

6.   2% Sodium Silicofluoride by weight.

After grinding an appropriate mixture of raw materials without flux, it is proposed to first find out if cement can be formed at 1350°C when fired for 1 hour. If successful, it

is proposed to add the various fluxes, one at a time in order to study their effects with respect to the various cementitious phases formed in crude quantitative terms using X-ray analysis, 3 days and 7 days cured tensile strength, workability, stability, tap density, and colour.

It is also proposed to study the effect of heat treatment of clinkers on the above mentioned properties of the cements. For that three different rates of cooling were given --fan cooled, air cooled and furnace cooled.

The effect of the raw material morphology, such as slaked lime from different sources, rice husk ash of different colours and bayer's alumina of different reactivity, on the above mentioned properties of the cements is also proposed to be studied.

From the above studies it is hoped to obtain the best raw feed mix for the white portland cement. Using this composition it is proposed to study the effect of burning temperature and the holding time on the above mentioned properties of the cements.

The above study is expected to lead us to the lowest energy route for the white portland cement production. Using this route the cement is then synthesised in bulk for the usual routine property test.

Here in this chapter the literature survey is confined
to the study of general purpose ordinary portland
cement with occasional references to white portland
cement. After first discussing what a portland cement
is as per the I.S.Specifications, based on the massive
amount of literature available, we study the oxide
composition of cement raw feed, phase composition of
cement, structure and characteristics of the cementing
phases, sources and morphology of the raw materials,
design of the cement mix, calculation of the phase
composition, mixing and grinding of the raw materials,
burning operation in the kiln, heat analysis during
the cement formation, reaction kinetics, compound
saturation effect and the role of the mineralizers,
heat treatment of the clinkers, grinding of the
clinkers and finally the storage of the cement.

2.1 INTRODUCTION:

Before attempting to find an altogether new, low
energy route for the production of white portland cement,
it is essential to get familiar with the science of port-
land cement manufacturing first.

Broadly speaking, there are 5 types of portland
cements. The ordinary general purpose portland cement is
refered to as portland cement type I. Portland cement is
a fine blend of certain calcium silicates, calcium aluminates
and calcium alumino-ferrites which sets and hardens under
water. White portland cement is more or less similar to

ordinary gray portland cement. While ordinary portland cement has to satisfy the stipulations laid down in I.S. Specification: 269-1976, the white portland cement has to satisfy the stipulation laid down in I.S. Specification: 8042-1978. These requirements should be complied with when tested in accordance with I.S. Specification : 4031-1968 and IS Specification: 4032-1968.

2.2 WHAT IS ORDINARY PORTLAND CEMENT AS PER THE I.S. SPECIFICATION:

The I.S. Specification: 269-1976 does not directly discribe the ordinary portland cement through a neat, comprehensive defination. Instead it defines the portland cement through certain stipulations laid down for the chemical and physical requirements for cement. The specification also covers in short the manufacture, storage, sampling, rejection etc.

In order to ensure that there is no free unreacted lime, as it might lead to unsoundness, the I.S. Specification lays down the following stipulation for the oxide content of the raw feed,

$$\frac{wt.\% \ CaO \ - \ 0.7 \ wt.\% \ SO_3}{2.8 \ wt.\% \ SiO_2 + 1.2 \ wt.\% \ Al_2O_3 + 0.65 \ wt.\% \ Fe_2O_3}$$

should not be greater than 1.02 and should not be less than 0.66. It also states that $wt.\% \ Al_2O_3 \ / \ wt.\% \ Fe_2O_3$ should not be less than 0.66, because otherwise due to excess C_2S, the setting time for the cement is adversely effected. For

detailed discussion refer to section 2.14 under the sub-heading of magnesium oxide.

In order to ensure that sufficient hydration and hence sufficient development of strength takes place, the I.S. Specification states that the wt.% insoluble residue and wt.% of total loss on ignition should not exceed 2% and 5% respectively. Whenever partial hydration of stored cement takes place the ignition loss increases.

In order to ensure that long term unsoundness does not take place, the I.S. Specification restricts magnesia content to below 6% by mass. For details refer to section 2.14 under sub-heading of magnesium oxide.

I.S. Specification also stipulates that the total sulphur content, calculated as wt.% SO_3, should not exceed 2.75% when wt.% C_3A is less than or equal to 7%; and that it sould not exceed 3% by weight when wt.% C_3A is greater than 7%. Otherwise sulphur gives rise to the formation of excess $CaSO_4$, which acts as a retarder of the setting time and which, in the absence of MgO and in the presence of C_3A, affects the formation C_3S adversely. Besides $CaSO_4$ causes expansion, not through hydration, but through the formation of calcium sulphoaluminate.

The alkali content, i.e. wt.% $(Na_2O + K_2O)$ is restricted below 0.6% because the alkali tends to react with the reactive siliceous aggregates, containing up to 15%

Because Mn_2O_3 tends to substitute Fe_2O_3 in solid state ferrites, thereby causing deteroriation of strength, the manganese oxide is restricted to below 5% by mass.

Phosphate tends to enter into solid solution with C_2S, thereby adversely affects the formation of C_3S. This leads to erratic rate of set and retardation in development of strength. Therefore P_2O_5 is restricted below 2.25% by mass. For details refer to section 2.14 under the sub-heading of Calcium phosphate.

Then, as already mentioned, there are certain physical requirements laid down for portland cement. The specific surface area should not be less than 2250 cm^2/gm. Otherwise sufficient strength does not get developed. For details refer to section 2.16.

In order to ensure that the cement mortar does not develop undue cracks, the expansion for unaerated cement, with less than 3 wt.% MgO, when tested by 'Le Chetelier' method, is limited below 10 mm. While expansion for unaerated cement, with more than 3 wt.% MgO, when tested by autoclave method is restricted below 0.8%.

If cement sets too fast the workability of the cement sand mortar is adversely hampered. But then, if it sets too slowly, then the speed of construction is adversely hampered. So the I.S. Specification stipulates that the initial setting time should not be less than 30

minutes and the final setting time should not be greater than 600 minutes, as tested by Vicat's apparatus.

Compressive strength development is the most important parameter for portland cement. So the I.S. Specification states that when tested in accordance with I.S:4031-1968, the compressive strength of 5 cm x 5 cm x 5 cm 1:3 cement sand cube, should not be less than 160 kgf/cm^2 and 220 kgf/cm^2 after 72 $\pm$ 1 hour and after 168 $\pm$ 2 hours respectively. It also states that, not with standing the strength requirements, the cement must also show a progressive increase in strength from that obtained at 72 hours.

No specific value for tensile strength is required for portland cement. By agreement between the purchaser and the manufacturer, the transverse strength test of the plastic mortar may be specified and the permissible values will have to be mutually agreed upon to between them.

2.3 REQUIREMENTS FOR WHITE PORTLAND CEMENT AS PER
I.S. SPECIFICATION:

The I.S. Specification: 8042-1978 states that, when tested in accordance with the methods given in I.S:4032-1968, white portland cement shall comply with the chemical requirements laid down for the ordinary portland cement in IS:269-1976, with the additional proviso that iron oxide (Fe_2O_3) shall not be more than 1% and the requirement of total loss on ignition be deleted.

The I.S. Specification states that the physical requirements for the white portland cement, shall be as laid down in I.S: 269-1976, except that, compressive strength of the mortar prepared from white portland cement shall not be less than 90% of that specified for ordinary portland cement.

Besides the I.S. Specification also lays down the stipulation for the degree of whiteness of white portland cement. It says that'heap some quantity of dry neat cement into a mold of the shape of a ring of 39 mm diameter and 3mm height placed on a clean glass plate, and gently press it down with another clean glass plate, so that the density of the cement compact is close to that of the standard magnesium oxide blocks.' After preparing two such specimens one is asked to compare the reflectivity of the compact cement surface with standard magnesium oxide blocks of certified reflectivity, on absolute scale, with the help of a reflectometer or reflectance spectrophotometer. The average reflectance of the two cement specimens should not be less than 70%, and the reflectance value of the 2 cement specimens, should not differ by more than two unit.

2.4   OXIDE COMPOSITION OF ORDINARY AND WHITE PORTLAND CEMENT:

The limits of composition for the ordinary portland cement raw feed mix are approximately as given in the next page.

wt.% CaO	60 to 67
wt.% SiO_2	17 to 25
wt.% Al_2O_3	3 to 8
wt.% Fe_2O_3	0.5 to 6
wt.% MgO	0.1 to 5.5
wt.% $(Na_2O + K_2O)$	0.5 to 1.3
wt.% SO_3	1 to 3

A typical oxide composition for white portland cement raw feed mix is given below:

wt.% CaO	65.0
wt.% SiO_2	25.5
wt.% Al_2O_3	5.9
wt.% Fe_2O_3	0.6
(includes FeO as Fe_2O_3)	
wt.% MgO	1.1
wt.% $(Na_2O + K_2O)$	0.6
wt.% SO_3	0.1
	98.8

2.5 PHASE COMPOSITION OF ORDINARY PORTLAND CEMENT:

As already mentioned ordinary portland cement is basically a mixture of tricalcium silicates, dicalcium silicates, tricalcium aluminates, tetra-calcium alumino-ferrites alongwith little amounts of gypsum, magnesia and free lime. A typical phase composition is given in the next page.

wt.% C_3S	45.0
wt.% C_2S	27.0
wt.% C_3A	11.0
wt.% C_4AF	8.0
wt.% $CaSO_4$	3.1
wt.% MgO	2.9
wt.% free CaO	0.5

2.6 STRUCTURES AND CEMENTING CHARACTERISTICS OF VARIOUS PHASES IN PORTLAND CEMENT:

2.6.1 Tricalcium Silicate (also called Rankinite)

The structure is either hexagonal or pseudo-trigonal. The hexagonal structure was reported by Andersen and Lee (3) and Danial and Hellner (4). The unit cell dimensions as reported by these investigators, respectively are given below:

$$a = 7.0 \text{ Å} \quad , \quad C = 25.0 \text{ Å} \quad , \quad \text{and}$$
$$a = 7.078 \text{ Å} \quad , \quad C = 24.940 \text{ Å}.$$

The pseudo-trigonal structure was reported by Jeffery (5). The unit cell dimensions as reported by him are

$$a = 7.0 \text{ Å} \quad , \quad C = 25.0 \text{ Å}.$$

The most prominent d-values are (4a):

2.770 Å (very strong) – but clashes directly with 2.770 Å of C_3A(weak).

2.730 Å (very strong) – but clashes directly with 2.730 Å of β C_2S (very strong).

$3.020 \overset{\circ}{A}$ (strong) — nearest being $3.030 \overset{\circ}{A}$ of C_3A (weak),
$3.030 \overset{\circ}{A}$ of βC_2S (weak broad) and
$3.000 \overset{\circ}{A}$ of γC_2S (strong).

$2.178 \overset{\circ}{A}$ (strong) — nearest being $2.180 \overset{\circ}{A}$ of C_5A_3 (strong),
$2.182 \overset{\circ}{A}$ of βC_2S (strong) and
$2.170 \overset{\circ}{A}$ of   MF (medium).

Tricalcium silicate is prepared from $CaCO_3 + SiO_2$ at 1500°C. It melts incongruently at 1900°C. It is stable between 1300°C and 1900°C. At 1900°C it dissociates into $CaO + \alpha C_2S$ and at 1300°C into $CaO + \beta C_2S$. At ordinary temperatures it exists in a metastable state.

Tricalcium silicate has all the essential properties of the portland cement. It undergoes an initial and final set within a few hours after gauging and, when properly prepared, it shows no unsoundness. Strain produced inthe crystal lattice by entry of C_3A and MgO , changes its reactivity with water. When mixed with water it is normally/ less plastic than portland cement, so more water is required for obtaining a workable paste. The addition of gypsum renders it more plastic and has some effect on the setting time. Both acceleration and retardation of set have been reported.

The compressive strength development of C_3S neat specimen is shown below in kgf./cm^2. (6)

	7 days	28 days	180 days	365 days
C_3S	322	466	512	584

2.6.2 α - Dicalcium Silicate (also called Nagelschmidtite)

The structure is hexagonal. This has been reported by Greene (7), by Bredig (8), by Douglass (9), by Midgley (10). They have however, reported different values for the unit cell dimensions. The values reported by them, are respectively given below:

$$a = 5.40 \overset{o}{\text{A}} \quad , \quad c = 7.00 \overset{o}{\text{A}} \; ;$$
$$a = 5.45 \overset{o}{\text{A}} \quad , \quad c = 7.18 \overset{o}{\text{A}} \; ;$$
$$a = 5.46 \overset{o}{\text{A}} \quad , \quad c = 6.76 \overset{o}{\text{A}} \; ;$$
$$a = 21.80 \overset{o}{\text{A}} \quad , \quad c = 21.54 \overset{o}{\text{A}} \; .$$

The most prominent d–values are (4a):

2.70 $\overset{o}{\text{A}}$ (very strong) – nearest being 2.69 $\overset{o}{\text{A}}$ of C_3A (very strong), 2.69 $\overset{o}{\text{A}}$ of C_2F (strong), 2.72 $\overset{o}{\text{A}}$ of KA (very strong), 2.73 $\overset{o}{\text{A}}$ of γC_2S (very strong) and .2.70 $\overset{o}{\text{A}}$ of C_3S (very strong).

2.81 $\overset{o}{\text{A}}$ (strong) – nearest being 2.82 $\overset{o}{\text{A}}$ of βAl_2O_3 (strong), 2.78 $\overset{o}{\text{A}}$ of $\beta'' C_2S$ (very strong), 2.77 $\overset{o}{\text{A}}$ of C_3A (very strong), 2.77 $\overset{o}{\text{A}}$ of C_4F (strong) and 2.778 $\overset{o}{\text{A}}$ of CaO (medium).

α - Dicalcium Silicate is prepared from βC_2S + Na_2O + Al_2O_3 (or Fe_2O_3) at 1450°C. It melts congruently at 2130°C. It is stable above 1420°C – 1447°C. On cooling it changes reversibly to the α form. If a foreign element is more soluble in the high temperature enantiotropic form than in the lower temperature form, the inversion temperature is reduced by its presence. In pure form the

inversion temperature is 1456°C $\pm$ 2.2°C. But addition of excess of 0.19% SiO_2 lowers it to 1438°C. With Na_2O + Fe_2O_3 in solid solution it is 1175°C and with Na_2O+ Al_2O_3 it is 1180°C. Inversion rate is very fast. But then if it is in the form of solid solution with other compounds then it may be retained at room temperature by and extremely fast cooling rate. For optimum retention it should contain either 4.2% Na_2O with 5.6% Fe_2O_3 or 2.8% Na_2O with 3.8% Al_2O_3.

It exhibits no definite setting time and the guaged mass sets only slowly over a period of some days. When statilized to the room temperature by using tricalcium phosphate this polymorph has no cementing properties.

2.6.3 α - Dicalcium Silicate (also called Bredigite)

Though the structure has been agreed to be orthorhombic, but then widely varying values of unit cell dimensions have been reported. The values reported by Bredig (8) and Douglass (9) respectively are given below:

a = 5.30 Å,   b = 9.55 Å,   c = 6.78 Å ;

a = 10.91 Å.   b =18.41 Å,   c = 6.76 Å .

The most important d-values are (4a);

2.76 Å (very strong) - nearest being 2.77 Å of C_3S
(very strong), 2.77 Å of C_3A
(weak), 2.77 Å of C_4AF (strong) .
and 2.74 Å of γ C_2S (very strong).

2.750 $\overset{o}{A}$ (very strong) – but clashes directly with 2.750 $\overset{o}{A}$ of $KC_{23}S_{12}$ (very strong, broad), and 2.750 $\overset{o}{A}$ of γAl_2O_3 (medium).

2.690 $\overset{o}{A}$ (very strong) – but clashes directly with 2.69 $\overset{o}{A}$ of C_3A (very strong) and 2.690 $\overset{o}{A}$ of βAl_2O_3 (very strong).

2.200 $\overset{o}{A}$ (strong) – but clashes directly with 2.000 $\overset{o}{A}$ of Fe_2O_3 (medium) and 2.200 $\overset{o}{A}$ of C_3A (medium).

2.035 $\overset{o}{A}$ (strong) – nearest being 2.033 $\overset{o}{A}$ of C_3A (weak), 2.030 $\overset{o}{A}$ of βAl_2O_3 (strong) and 2.020 $\overset{o}{A}$ of $\beta-C_2S$ (weak).

α' – Dicalcium Silicate is prepared from $\beta -C_2S$ by quenching it from 1750°C. The transition occurs at about 1450°C. It is stable from 800°C to 1447°C, on heating, starting with the γ form, but on cooling it persists down to about 650°C where it inverts reversibly to the β-form. It can be stabilized to the room temperature by addition of 15 wt.% of tricalcium phosphate, the two compounds forming solid solution. When stabilized in this way the polymorph is only weakly hydraulic.

2.6.4 $\underline{\beta - Dicalcium\ Silicate\ (also\ called\ Larnite)}$

The structure is monoclinic as reported by Midgely (11). She reported the unit cell dimensions to be;

$a = 5.48\ \overset{o}{A}$, $b = 6.76\ \overset{o}{A}$, $c = 9.28\ \overset{o}{A}$

$$\beta = 94°\ \ 33'.$$

The most important d-values are (4a);

2.780 $\overset{o}{A}$ (very strong) – nearest being 2.778 $\overset{o}{A}$ of CaO(very strong), 2.810 $\overset{o}{A}$ of αC_2S(strong).

2.730 $\overset{o}{A}$ (very strong) – but clashes directly with 2.73 $\overset{o}{A}$ of C_3S (very strong)

2.610 $\overset{o}{A}$ (strong) – but clashes directly with 2.610 $\overset{o}{A}$ of γ C_2S (weak).

2.182 $\overset{o}{A}$ (strong) – nearest being 2.180 $\overset{o}{A}$ of C_5A_3 (strong), 2.178 $\overset{o}{A}$ of C_3S(strong), 2.185 $\overset{o}{A}$ of $KC_{23}S_{12}$(medium), 2.190 $\overset{o}{A}$ of C_4AF (medium) and 2.190 $\overset{o}{A}$ of γ C_2S (weak).

β – Dicalcium Silicate is prepared from Ca CO_3 + SiO_2 at 1350°C. The transition point is however at 675°C. In the pure binary CaO-SiO$_2$ system, β-form is unstable at all temperature. Till 650°C, on cooling α'-form is stable, and below 670°C onwards, γ-phase is stable. So if the β – phase has to form from α'-phase at a temperature below 670°C it has to be necessarily a metastable phase. But then in a polycomponent system, it may form a stable phase of primary crystallization at a certain temperature due to the presence of the additional components.

But.nevertheless, evern the metastable β-phase does form because the α' to γ inversion is inhibited due to the large volume change required. In the α' form the

coordination number of Ca ion for oxygen is 10 or 9, for β- orm it is 8 and for γ- form it is 6. Change of α' -form to γ-form involves a large scale atomic rearrangements with a 12% volume increase and the specific gravity changes from 3.4 to 3.17. This inhibits the inversion, because at 670°C, the monotropic β- form can be produced is a metastable phase with just 1% volume increase only. This inversion is easily avoided for many many months if the charge is cooled rapidly. With rapid quenching , layers of glass are formed around the grains of β- C_2S and so mere physical pressure created on the crystal grains blocks the inversion wave. A very small addition of B_2O_3 or Cr_2O_3 helps the process.

Once the pure β -phase has been formed, on cooling however to about 520°C, it inverts to γ- form. This inversion temperature can be made to vary over a range. In presence of certain impurities it can be delayed indefinitely.

β- Dicalcium silicate has no definite setting time. It sets very slowly. It produces little strength uptil 28 days. Thereafter it gains strength steadily until it approaches the initial strength of C_3S as can be seen from the following table;

Compressive strength of neat specimen in Kgf./cm^2 (6)

	7 days	28 days	180 days	365 days
-C$_2$S	24	42	193	325

The addition of gypsum produces little change.

2.6.5 γ- Dicalcium Silicate (also called Shannonite)

The crystal structure is orthorhombic. This has been reported by Daniel and Tscheischwil (12). They have reported the unit cell dimensions to be

a = 5.06 Å   b = 11.28 Å   c = 6.78 Å.

The most important d-values are (4a);

2.740 Å (very strong)- nearest being 2.75 Å of γ-Al$_2$O$_3$ (medium), 2.75 Å of KC$_{23}$S$_{12}$ (very strong, broad), 2.73 Å of C$_3$S (very strong) and 2.73 Å of β-C$_2$S (very strong).

3.000 Å (strong)   - nearest being 3.020 Å of C$_3$S (strong), 3.035 Å of CaCO$_3$ (very strong) and 2.980 Å of C$_5$A$_3$ (strong).

1.905 Å (strong)   - but clashes directly with 1.905 Å of C$_3$A (strong).

γ- Dicalcium Silicate is prepared from CaCO$_3$+ SiO$_2$ at 1400°C. The transition point occurs at about 850°C. When it is formed from the β - phase at about 675°C through an inversion process, due to accompanying increase in volume, the crystal mass falls apart into a

fine powder, known in cement industry as dusting. This phase is stable below 725 to 830 °C, above which it inverts to the α' - form.

γ- Dicalcium Silicate neither sets nor hardens when mixed with water.

2.6.6 Tricalcium Aluminate:

The crystal structure is cubic. This has been reported by Bussem (13) and Fred Ordway (14). They reported the unit cell dimension to be

$$a = 15.2 \overset{\circ}{A}$$

The most prominent d-values are (4a);

2.690 $\overset{\circ}{A}$ (very strong) - but clashes directly with 2.690 $\overset{\circ}{A}$ of C_2F (strong), 2.690 $\overset{\circ}{A}$ of β-Al_2O_3 (very strong) and 2.690 $\overset{\circ}{A}$ of Fe_2O_3 (very strong).

1.554 $\overset{\circ}{A}$ (very strong) - nearest being 1.551 $\overset{\circ}{A}$ of MA(very strong) and 1.558 $\overset{\circ}{A}$ of C_2F (medium) and 1.558$\overset{\circ}{A}$ of NC_8A_3(very strong).

1.905 $\overset{\circ}{A}$ (strong) - but clashes directly with 1.905 $\overset{\circ}{A}$ of γ - C_2S (strong).

1.354 $\overset{\circ}{A}$ (strong) - nearest being 1.353 $\overset{\circ}{A}$ of C_5A_3 (weak) and 1.355 $\overset{\circ}{A}$ of γ - C_2S (weak).

Tricalcium aluminate is prepared from $CaCO_3$+ Al_2O_3 at 1375°C. It melts incongruently at 1535°C dissociating into CaO and liquid of composition of 57.2 wt.% CaO and

Tricalcium aluminate produces some strength in 1 day. But it shows no subsequent development of strength. It only gives a flash set with water — accompanied with excessive steaming. Even moist air can set it. After breaking the initial set it again becomes plastic. For getting a normal setting time 15% gypsum and 50% water has to be added to it.

Its cementing capacity is doubtful. Its value is mainly limited in rendering burning possible by acting as a flux. It removes many difficulties of the pure CaO — SiO_2 binary system. Anyway the compressive strength in $Kgf./cm^2$ of neat specimen can be seen from the following table; (6)

	7 days	28 days	180 days	365 days
C_3A	118	125	0	0

2.6.7 Penta – calcium trialuminate:

This phase has often been mixed up with $C_{12}A_7$. The difference in their composition is small, as can be seen from below:

C_5A_3	47.78 % CaO,	52.22% Al_2O_3
$C_{12}A_7$	48.53 % CaO,	51.47% Al_2O_3.

Penta-calcium trialuminate is an unstable phase.

Most prominent d-values are (4a);

2.670 $\overset{o}{A}$ (very strong) – nearest being 2.680 $\overset{o}{A}$ of NA (strong),

$\qquad$ 2.680 $\overset{o}{A}$ of NC_8A_3 (very strong) and

$\qquad$ 2.630 $\overset{o}{A}$ of C_4AF (very strong).

2.980 $\overset{o}{A}$ (strong) – $\qquad$ nearest being 2.950 $\overset{o}{A}$ of MF (medium),

$\qquad$ 3.000 $\overset{o}{A}$ of $\gamma - C_2S$ (strong).

This phase does not give rise to flash set. Initial set takes place in 3 to 5 minutes and final set in 15 to 30 minutes – the latter being accompanied by evolution of much heat. Gypsum can ret i' only the final set by about 1 hour and it increases the strength by 50 to 100%. The compressive strength of the neat specimen in Kgf./cm^2 can be seen from the following table (6);

	7 days	28 days
C_5A_3	123	91

2.6.8 Tri-calcium penta – aluminate:

It was thought to be the composition of a phase now identified as CA_2. Tricalcium penta–aluminate is said to be one of the cementing compounds in the high alumina cements. It is a mixture of CA and CA_2. Since pure CA_2 has no cementing value, the considerable strength which C_3A_5 develops is attributed to the CA portion of it.

2.6.9 Calcium monoaluminate:

This crystal system is probably monoclinic but sometimes the crystals are markedly pseudo hexagonal. It crystallizes in irregular grains, sometimes prismatic. Twining is characteristic.

It is one of the main contituents of high alumina cement. It does not suffer from rapid setting. Initial set is in 25 minutes and the final set is in 2 hours. Rapidly it attains a high strength. The compressive strength of neat specimen in $Kgf./cm^2$ can be seen from the following table (6);

	7 days	28 days	90 days
CA	418	265	277

Addition of gypsum lowers the strength and accelebates the set.

2.6.10 Tetra - calcium alumino - ferrite:
(also called Brownmillerite)

The crystal structure is orthorhombic. This has been reported by Bussem (13). The reported value of the unit cell dimensions are

$$a = 5.34 \overset{o}{A}, \quad b = 14.44 \overset{o}{A}, \quad c = 5.52 \overset{o}{A}.$$

The most prominent d-values are (4a):

$2.630 \overset{o}{A}$ (very strong) - but clashes directly with $2.630 \overset{o}{A}$

of $KC_{23}S_{12}$ (weak).

29.

2.770 $\overset{o}{A}$ (strong) — but clashes directly with 2.770 $\overset{o}{A}$ of C_3S (very strong).

2.030 $\overset{o}{A}$ (strong) — but clashes directly with 2.030 $\overset{o}{A}$ of $\beta - Al_2O_3$ (strong), 2.030 $\overset{o}{A}$ of $\gamma - Al_2O_3$ (strong) and 2.030 $\overset{o}{A}$ of NC_8A_3 (weak).

1.808 $\overset{o}{A}$ (strong) — nearest being 1.805 $\overset{o}{A}$ of NA (weak), 1.805 $\overset{o}{A}$ of $KC_{23}S_{12}$ (weak), 1.800 $\overset{o}{A}$ of $\gamma - C_2S$ (medium), 1.800 $\overset{o}{A}$ of $\beta - C_2S$ (medium) and 1.821 $\overset{o}{A}$ of C_3A (weak).

1.572 $\overset{o}{A}$ (strong) — nearest being 1.575 $\overset{o}{A}$ of $\beta - C_2S$ (weak), 1.569 $\overset{o}{A}$ of $\beta - Al_2O_3$ (strong), 1.567 $\overset{o}{A}$ of KA (strong).

Tetra — calcium alumino— ferrite is prepared from $Ca\,CO_3 + Al_2O_3 + Fe_2O_3$ at 1345°C. It melts congruently at 1415°C. It appears as crystals only if iron is in large quantity and the cooling rate is slow.

Tetra-calcium alumino-ferrite hydrates rapidly. There is no flash setting. There is a marked heat evolution through less than that observed with C_3A. The compressive strength of the neat specimen in Kgf./cm^2 is shown below (6):

	7 days	28 days	180 days	365 days
C_4AF	300	384	493	595

2.6.11 Di-calcium ferrite:

The crystal structure is orthorhombic as reported by Bussem (13).

The most prominent d-values are (4a):

1.940 Å (very strong) — nearest being 1.936 Å of β-Al_2O_3
(stro   (strong) and 1.943 Å of C_5A_3 (strong).

1.840 Å (strong)   — but clashes directly with 1.840 Å
                            of NC_8A_3 (weak).

1.585 Å (strong)   — nearest being 1.587 Å of $CaCO_3$ (weak),
                            1.579 Å of α - C_2S (medium) and
                            1.572 Å of C_4AF (strong).

Di-calcium ferrite is prepared from $CaCO_3$+ Fe_2O_3 at 1425°C. It melts congruently at 1435°C. Di-calcium ferrite sets and hardens rapidly but without the flash set or marked heat evolution. But continuous expansion after setting eventually disrupts the set material.

2.7 SOURCES AND MORPHOLOGY OF RAW MATERIALS:

Bulk of the raw materials are the argillaceous and calcareous materials. Principal available forms of argillaceous materials are clay, shale, slate, blast furnace slag, ashes etc. Claystone is indurated sedimentary rock—mostly hydrous alumino-silicates. Shale is laminated or fissile clay stone but more consolidated. Slate is metamorphosed form of clay.

The principal available sources of calcareous materials are limestone, chalk, marl, marine shell, alkali wastes etc., While chalk is formed from the shells of minute marine organisms, marl is formed in some fresh water lakes, by action of some acquatic plants. Plants extract CO_2 for photosynthesis from bicarbonate in water there by locally reducing the solubility of

$CaCO_3$ near the leaves, where it gets precipitated as friable scales known as marl. Marlstone is indurate, non-fissile, blocky and massive rock formed out of friable marl. Alkali waste could either be precipitated $CaCO_3$ obtained as waste product in the manufacture of NaOH by the Le Blanc Process or it could be $Ca(OH)_2$ obtained as waste product during the manufacture of acetylene.

Whenever the alumina content is low in the argillaceous materials, extra alumina is required in the form of bayer's alumina.

Clay contain iron, alkali and alkaline earth metals. Since iron leads to intense colouration, for white portland cement, the clay should be very low in iron. Final cement has to contain less than 0.6% alkalies and 6% MgO. So clay should not introduce excess of either alkalies or alkaline earth metals.

Normally blast furnace slag introduces Mn_2O_3. Since Mn_2O_3 substitubes for Fe_2O_3 in solid state ferrites, thereby unfavourably effecting the strength, the slag should be low in Mn_2O_3.

The lime stone should not be high in MgC_3. Nor should it contain seams of gypsum or pyrite because there is a limitation on $CaSO_4$ content in cement. If high grade limestone, which requires great power for grinding, cannot be avoided, then shale should be added to soften it. Flint pebbles must be removed from chalk and excessive silica sand from the marl.

2.8 DESIGN OF CEMENT MIX:

The design and control of feed composition during the process of manufacture is very important because with each 1% increase in $CaCO_3$ content the potential C_3S is increased by 14.2% and C_2S is decreased by 13.5%. Addition of 1% of a typical coal ash lowers C_3S by 6.5% and raises C_2S by 5.6%. If dust loses are also considered then C_3S is decreased and C_2S is increased by 15% or more. If 1% MgO is substituted for CaO, on an unignited basis, C_3S is increased by 16.4% and C_2S is decreased correspondingly.

Now the design and control of the feed composition is very difficult because the raw mix consists of a large number of consitutents whose purity level keeps on varying from batch to batch. Besides the burning operation gives incomplete combination and cooling rate gives incomplete crystallization. Besides precision methods cannot be used for large tonnage handled.

Basically there are two principles used for chemical control. One is based on the control of the potential C_3S and C_2S as determined from the phase composition equations. The other is based on lime-deficiency method. Lime deficiency is the amount of CaO which must be added to any given raw mixture in order to cause all the SiO_2 to combine as C_3S leaving zero C_2S. Therefore CaO present + lime deficiency = theoretical lime limit to form the compound of maximum lime content from all the oxides capable of combining with lime. Higher the C_2S in clinker, higher is the lime deficiency, since C_2S alone is capable of taking up more CaO.

Lime deficiency (ds) $\propto$ C_2S

$$\frac{C_2S}{ds} = \frac{\text{mol. wt. of } C_2S}{\text{mol. wt. of CaO}}$$

Therefore   ds = 0.3256 C_2S.

Using this method the lime deficiency (ds) is controlled.

But Dahl (15) introduced the concept of technical lime deficiency(dr). Now

$$dr = 0.3256 \ C_2S - 0.178 \ C_3A.$$

As the C_3A content is decreased, the minimum safe value of C_2S is also decreased. So in a low C_3A compositions a higher C_3S may be secured, without passing the technical lime limit. But then C_3A potential is nearly constant in most of the plants. So constant dr or ds means a constant C_2S.

Based on lime deficiency, the design relationship is(16)

$$P = p - 0.23 \ (D-d)$$

where   P = % $CaCO_3$ required,

p = % $CaCO_3$ actually present,

D = desired lime deficiency,

d = actual lime deficiency in the raw material.

This lime-deficiency method is better because here all the constituents, including the minor ones, react at clinkering temperature and therefore are accounted for by the test procedure. Besides time is shortened between the moment the sample is taken from the raw mixture stream and moment when the text results can be applied.

Based on these principles many proportioning
formulae have been suggested by various investigators. We
have proportioning formulae of Le Chatelier (17); of S.B.
and W.B. Newbery (18); of Hendrickx (19); of Duchez (20);
of Forsen (21); of Budnikov and Strelkov (22); of Lea and
Parker (23). We also have Hydraulic index of Vicat (24),
the Hydraulic modulus of Michaelis (25), the Lime saturation
value of Kuhl (26) and Cementation index of Eckel (27).

In 1916, S.B. Newberry modified slightly the earlier
formulae, in accordance with his acceptance of the work
reported by Rankin (28). He gave a final practical formula
given below,

$$CaO \ = \ 2.5 SiO_2 + 1.6 \ Al_2O_3 \ .$$

He urged a lime factor expressed by the relation,

$$\frac{CaO - 1.6 \ Al_2O_3}{SiO_2} \ = \ 2.5.$$

and said "it will give cements of practically maximum quality
with any material whether siliceous or aluminous, provided
the mix is finally ground and properly burned." Newberry's
formula was modified by Eckel(27) in 1922. He called the
ratio,

$$\frac{2.8 \ SiO_2 + 1.1 \ Al_2O_3 + 0.7 \ Fe_2O_3}{CaO \ + \ 1.4 \ MgO}$$

cementation index, and in a properly proportioned cement,
he felt that this index must be 1.0, or slightly higher for
the purpose of safety.

In 1929, Kuhl (26) proposed the ratio,

$$\frac{CaO - (CaO \text{ in } CaSO_4)}{2.8 \ SiO_2 + 1.1 \ Al_2O_3 + 0.7 \ Fe_2O_3} = 1$$

as the correct value, and called it lime saturation of the
mixture. But in 1935 when Lee and Parker (23) approached
this problem from the theoretical considerations they found,

Limiting $CaO = 2.80 \ SiO_2 + 1.18 \ Al_2O_3 + 0.65 \ Fe_2O_3$

when $A/F > 0.64$.

Many of the earlier equations derived from practical conside-
rations approached this equation very closely.

In 1946 Budnikov and Str lkov (22) found that,

CaO limit $= 2.8 \ SiO_2 + Al_2O_3 + 0.7 \ Fe_2O_3$

when $A/F > 2$, and

CaO limit $= 2.8 \ SiO_2 + 1.65 \ Al_2O_3 + 0.35 \ Fe_2O_3$

when $A/F < 2$.

2.9   CALCULATION OF THE CEMENTING PHASE COMPOSITION:

Once the raw feed has been proportioned, based on
that, one can calculate the theoretical equilibrium crystalli-
zed phase composition of portland cement. For this the
knowledge of equilibrium crystallization in $CaO-MgO-Al_2O_3-$
$Fe_2O_3- SiO_2$ system is essential.

It is known that first Fe_2O_3 reacts with Al_2O_3 and
CaO to form an iron phase which may lie between C_4AF and C_6A_2F
-- but generally it is taken as C_4AF. Then the Al_2O_3 remaining

from the above combination reacts with CaO to form C_3A. The
CaO remaining from the above two combinations reacts with SiO_2
to first form C_2S. Then any CaO further left over, reacts
with C_2S to form C_3S. If CaO remains even after converting
all the C_2S into C_3S, then it stays as uncombined CaO. The MgO
remains essentially uncombined.

The equilibrium crystallization, is however not
attanable in practice due to the coarse particles involved in
the solid - liquid phase reactions. Besides, the resolution
during cooling, of the previously crystallized phases, may
not be complete in some compositions or these phases may be
embedded in some other phases where liquid cannot act upon.
Again undercooling to glass also takes place. So our process
only constitutes the first approximation.

Accordingly to Lea and Parker's equations (23) which
was later extended by Dahl/$^{(29)}$ for the $C_3S- C_2S- C_3A - C_4AF$
system, the following relations give the proportion of various
cementing phases,

$$\text{wt.\% } C_3S = 4.0714 \text{ (wt.\% CaO)} - 7.5999 \text{ (wt.\% } SiO_2)$$
$$-6.7179(\text{wt.\% } Al_2O_3) - 1.4300 \text{ (wt.\% } Fe_2O_3)$$

$$\text{wt.\% } C_2S = 8.5999 \text{ (wt.\% } SiO_2) + 5.0679 \text{ (wt.\% } Al_2O_3)$$
$$-3.0714(\text{wt.\% SaO)} + 1.0788 \text{ (wt.\% } Fe_2O_3)$$

$$\text{wt.\% } C_3A = 2.6500 \text{ (wt.\% } Al_2O_3) - 1.6919 \text{ (wt.\% } Fe_2O_3)$$

$$\text{wt.\% } C_4AF = 3.0432 \text{ (wt.\% } Fe_2O_3).$$

2.10 MIXING AND GRINDING OF RAW MATERIALS:

At clinkerization temperature the portland cement is
not completely melted, but only sintered, so some reactions have

to take place by diffusion. If the different raw materials are not mixed uniformly and intimately, the reactions will not take place in a uniform manner throughout the mass. An aera of lime particles may be so far removed from a region of some acidic component, that these particles may remain unreacted in the mixture as free lime. This free lime will prove just as much disastrous in producing unsoundness as similar free lime that might be left due to an excess lime in an unproportioned mixture.

The ease with which the combination of various components can take place in the kiln, is strongly influenced by the fineness to which the raw mix is ground. Coarse particles of SiO_2 and $CaCO_3$ fail to react completely under commercial burning conditions. As reported by Heilmann (30) not more than 0.5% of SiO_2 particles above 0.2 mm size, or no more than 1% between 0.09 and 0.2 mm should be present in the raw mixes with Kuhl's lime saturation factor as high as 0.95, but that for a rather lower factor of 0.89 double these amounts may be permissible. Contents upto 5% of pure $CaCO_2$ particles above 0.15 mm in size could be tolerated without serious effect on the ease of burning, while with impure silicerus limestones the proportion of coarse particles would be higher. In 1957, Kramer (31) found that the maximum desirable size of limestone or quartz grain should be 0.1 mm.

The reaction of CaO with C_2S to form C_3S depends on the lime dessolving in the clinker liquid and must therefore be dependent on the rate of solution. This is controlled by

the size of the CaO particles which in turn is dependent on
the size of the limestone particles in the raw mix. As
reported by Toropov and Rumyantsev (32) the time required
for the solution is proportional to the particle diameter and
depends exponentially on the reciprocal of the absolute
temperature. The following equation holds approximately true,

$$\log t = \log \ D/A + 0.43 \ E/RT.$$

where t = time

D = particle diameter

A = constant

T = absolute temperature

E = activation energy = 146 Kcals./mol.

A similar form of relation was also found for the rate of
solution of quartz grain in the clinker liquid as reported
by Toropov and Rumyantsev (33).

The ease of burnability, i.e. combination of the
reacting phases, is more sensitive to the particle size of
quartz than those of lime or alumina. For details refer to
section 2.13, para no. 3.

In industry wet grinding is usually adopted because
close circuit grinding is preferred as practically no
advantage is accrued by over grinding. Closed grinding leads
to increased capacity of the plant and less fuel consumption.
Wet grinding also leads to better control of composition of
the kiln feed.

Finer the raw feed, lower is the burning temperature, but higher goes the grinding cost and the transportation cost of the finely grained slurry. Finer the raw material higher is the viscosity.

2.11 BURNING OPERATION IN THE ROTARY KILN:

Kiln feed is either dry powder, filter cake or a slury, fed in slowly and uniformly from the upper end of the kiln.

The kiln size is represented by the inside shell diameter and the nominal length. As per I.S. Specification; 8125-1976, rotary kilns can come in 6 sizes (A to F) with inside diameter varying from 9.514 ft. to 16.404 ft. and nominal length varying from 144.36 ft. to 278.87 ft. The kiln revolves at 1 to 0.5 RPM. Inclination is few tenths of an inch to the foot.

The clinkering temperature, as measured by optical pyrometers, varies for different raw materials from 1300°C to 1450°C, though occasionally it may fall outside these limits. Blast of powdered coal and air is introduced at the lower end. Theoretical temperature of the flame is above 2000°C. The actual flame temperature, which depends on the speed of combustion and other factors , has been ascribed various values upto 1700°C.

The time of passage of cement raw mix, through a rotary kiln 200 ft. long, is about 2½ hours. The time in the clinkering zone has been estimated to be 20 minutes or less. But the clinker is at its maximum temperature for even a shorter period. The temperature at which clinker emerges from the kiln is normally between 1200°C and 1400°C.

Clinker formation implies an increase in the liquid content sufficient to make the mix cohere into small balls. Compound formation need not proceed with the same rapidity. Since clinkering is dependent on the liquid formation, the minimum temperatures at which liquid forms in the raw mixes is of importance. Hansen (34) had given the following data for the minimum eutectic melting temperatures:

$$C_3S \ - \ C_2S \ - \ C_3A \hspace{3cm} 1455^\circ C$$

$$C_3S \ - \ C_2S \ - \ C_3A \ - \ Na_2O \hspace{2cm} 1430^\circ C$$

$$C_3S \ - \ C_2S \ - \ C_3A \ - \ Fe_2O_3 \hspace{2cm} 1340^\circ C$$

$$C_3S \ - \ C_2S \ - \ C_3A \ - \ MgO \hspace{2cm} 1375^\circ C$$

$$C_3S \ - \ C_2S \ - \ C_3A \ - \ Fe_2O_3 - MgO \hspace{1cm} 1300^\circ C$$

$$C_3S \ - \ C_2S \ - \ C_3A \ - \ Na_2O \ -$$
$$Fe_2O_3 - MgO \hspace{3cm} 1280^\circ C$$

The lowest temperature of 1280°C is not likely to be lowered appreciably further by the addition of any other minor components and is in good agreement with the various values of 1250°C - 1280°C reported on raw cement mixes. While almost all cement raw mixes are likely to show this same minimum temperature of liquid formation, the amount of liquid formed at this, and progressively higher temperatures, will depend on the proportion as well as the individual amounts of the minor components.

The clinkering range represents a range of liquid contents, varying from a minimum amount necessary to give a coherent clinker and a maximum amount where serious balling-up commences to occur. With high iron content, amount of liquid

formed increases rapidly with temperature thereby making clinkering range small. Clinkering range is also a function of the viscosity and surface tension of the liquid and of the manner in which these properties vary with the temperature. As reported by Endell and Hendrick (35) the viscosity at 1400°C was reduced by mixtures of upto 3% in the following order:

$$Na_2O < CaO < MgO < Fe_2O_3 < MnO$$
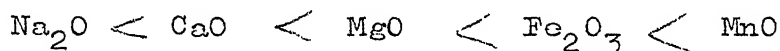
viscosity increases markedly with increase of SiO_2 and to a much less extent with the increase of Al_2O_3. Calcium fluoride in low concentration (0.7%) markedly decreases the viscosity, but in large amount it acts as a mineralizer promoting crystallization of the liquid (36). When it is used as a flux, the clinkering temperature is lowered and the liquid is initially more fluid, but the rapid onset of the crystallization stiffens the mass and the risk of formation of clinker rings is much reduced.

In a normal clinker the amount of liquid present at the clinkering stage is 20 to 30%.

Now we come to the course of the reactions in the rotary kiln. Evaporation of free water takes place at or below 100°C in the drying zone of the kiln, which constitute the first 1/3rd of the kiln. In the second 1/3rd of the kiln, which is a preheating zone, the organic matters burn off. We also have release of combined water from clay taking place at 500°C to 600°C.

Magnesium carbonate decomposes at about 600-700°C, but the temperatures reported vary considerably with the source of the material used.

From 800° to 900°C the limestone decomposes to CaO. When heated alone the vapour pressure of pure limestone reaches atmosphric pressure at 894°C.

In cement burning, the reaction between $CaCO_3$ and finaly divided quartz begin very faintly at as low a temperature as 600°C. It proceeds very slowly at 800°C forming CA, C_2F and C_2S. Between 800° and 900°C formation of $C_{12}A_7$ begins. Between 900° and 1100°C, C_2AS forms and decomposes again. Formation of C_3A and C_4AF also starts. All $CaCO_3$ gets decomposed and free lime reaches a maximum value. At 1100°C the reaction reaches appreciable speed. Between 1100° and 1200°C, formation of major part of C_3A and C_4AF takes place. Content of C_2S reaches a maximum. At around 1260°C the first liquid formation start. Between 1200° and 1450°C formation of C_3S takes place with progressive disappearance of free lime.

While the cementing phases are being formed, between 1100° and 1350°C volatization of alkalies also take place. The rate of volatization depends on the temperature. Addition of $CaCl_2 \cdot 2H_2O$ in the raw mix helps in the volatization of the alkalies. Holden (37) reported that the molecular sum of alkalies removed was approximately proportional to the amount of $CaCl_2$ added. Small addition of $CaCl_2$ removed greater proportions of potash than soda but, when the salt was added

in excess of 1.1%, the rate of soda removal increased
rapidly. Lower initial sulphate content also increases
alkali volatization.

2.12 HEAT ANALYSIS DURING THE BURNING OPERATION:

Heat is absorbed, or evolved in the following reactions
in cement formation;

Temperature	Reaction	Heat changes
100°C	Evaporation of free water	Endothermic
500°C & above	Evolution of combined water from clay.	Endothermic
900°C & above	Crystallization of amorphous dehydrated products of clay.	Exothermic
900°C & above	Evolution of CO_2 from $CaCO_3$	Endothermic
900°-1200°C	Reaction between lime and clay	Exothermic
1250°-1280°C	Commencement of liquid formation.	Endothermic
Above 1280°C	Further formation of liquid and completion of formation of cement compounds.	Probably endo-thermic on balance.

Evaporation of free water at 100°C requires 538 cals/
gm. The heat absorbed in dehydration of Kaolin, Montmorillonite
and Illite at 20°C, referred to water vapour is 262 cals./gm.,
94.6 Cals./gm. and 84.5 cals./gm. respectively. The product
of dehydration shows an exothermic reaction at about 900° to
950°C arrising from the crystallization of the amorphous
material, and it amounts in the case of dehydrated Kaolin to
72 ± 10 cals./gm. The heat absorbed in the dissociation of

$CaCO_3$ is 393 cals./gm. at 890°C. For $MgCO_3$ the values found by different investigators vary from 250 to 290 cals./gm. at 590°C. The reaction of the dehydrated clay products with lime is associated with a considerable evolution of heat : which varies with the cement composition and raw materials. It is about 100 to 120 cals./gm. for normal raw materials, but only about 50-70 cals./gm. when slag and limestone are used. A heat evolution of 100 cals./gm. is sufficient theoretically to raise the temperature o the reacting mases by over 300°C.

The heats of formation of the principal cement compounds and their specific heat data, needed in thermochemical calculation is given in literature (38). : . .:

As shown in Table Nos. 1.1 and 1.2 in section 1.1, the net theoretical heat required to form 1 kg. clinker from 1.55 kgs. dry calcium carbonate and clay is 420 Kcals. But then heat required in practice is, of course, considerably greater. With a modern wet process kiln the thermal efficiency is no much above 30%, but with special heat recuperators, value approaching 50% is obtained in the semi dry and dry processes. With shaft kilns the thermal efficiency is even higher. In ordinary rotary kiln, the fuel consumption is more than 1480 Kcals./kg. of clinker. For Lepol kiln, which is outstanding from the heat conservation point of view, the fuel consumption is about 1034 Kcals/kg. of clinker. Here the exit gas is utilized to heat a layer of pellitized raw mix that is spread out on a travelling grate. So we have a

double pass of the gases, first through a heated portion of
the mix and then through the moist pellets. The rotary kiln
into which the preheated pellets are discharged can be cut in
length by a half to a third, and the dust entering the stack
is said to be reduced to about 1.1 of the weight of the clinker.

The vertical shaft kiln is well adopted to small-scale
operation and is more economical with respect to fuel comsump-
tion. The initial problems of inhomogeneous clinker and non-
dependable cement qualities have been taken care of in the
modern designs. The modern shaft kiln is a conical shaped
shell, 26 ft. high, $9\frac{1}{2}$ ft. wide at the top and $7\frac{1}{2}$ ft. wide
at the bottom. The diminution in diameter with increasing
distance from the top allows for the contraction of the charge
during burning. Here more efficient methods of pellitizing
the raw material are used on whirling drums set at a sharp
diagonal. The capacity of these kilns is about 170 to 190
tons of clinker per day with the heat consumption of about
1000 Kcals./kg. of clinker. In-fact an interesting innovation
has been the use of a small shaft kiln to serve as a preheater
from which the partly burned clinker discharges into a short
rotary kiln for the completion of the reactions.

For a further detailed study on the heat balance of
the rotary kilns please refer to the literature (39 to 44).

As reported by Gygi (45) and Lysenko (46) electric
firing of rotary kilns was also tried in Switzerland during
the war of 1939-1945, using graphite electrode and a low tension
arc. About 946 Kcals. was required per kg. of clinker.

2.13 REACTION KINETICS DURING THE BURNING OPERATION:

Some compound formation reaction takes place between the solid and liquid phases and some between the adjacent liquid phases. Duration of the time required for the complete reaction depends upon;

a) Chemical composition of the raw mix,

b) Specific surface area of the raw material and perfection of dissemination of the several phases in the pulverized mixture of raw feed,

c) State of crystal lattice imperfections and formation of dissociation or inversion products at the clinkering temperature,

d) Uniformity of the raw mix,

e) Character of the reaction involved with the formation of the liquid (this is discussed in detail under the heading of compound saturation effect in section 2.14),

f) Lowest temperature for liquid formation and the amount of liquid formed (this is discussed in detail in sec. 2.14),

g) Temperature of clinkerization,

h) Rate of cooling. Too much of glass means too little of crystalline C_4AF and C_3A. (this is discussed in detail in section 2.15).

As reported by Hedvall (47) the velocity of the reaction in the solid state is given by,

$$velocity = A. \exp (-q/RT)$$

where A = constant depending on the texture of the material, particle size, conditions of contact etc. It is independent of the temperature.

R = Gas constant.

T = absolute temperature

q = energy of loosening of the lattice for the phase in question and of detaching a particle from its neighbour and to bring it to a state of reactivity.

In the burning zone of the kiln, the amount of solid phases formed is 70-75%. Hedvall has pointed out that the reaction velocity in the solid state are remarkably influence by changes in the state which the solids undergo at a given temperature. Alpha quartz, when transforming into crystobalite has a very low q value. This effect of the faulty lattice is so great that it surpasses by far the influence of specific surface area. If the lattice of both the solid phases can be made to become faulty at the same temperature, as by a transition of form, the acceleration of the reaction may become enormous.

The surface of a solid, being in a crystallographically imperfect state has a low q value. So higher the specific surface area the better. It has been found by Bogue (48) that the ease of burnability was more sensitive to the particle size of quartz than those of limestone or alumina. This is because unlike quartz, alumina enters into liquid state first and limestone, after dissociation, is already left in a porous condition with high specific surface area. More details on the effect of particle size on the burnability has already been given in section 2.10.

Nature of raw materials is also important. For instant if Al_2O_3 and SiO_2 are introduced in the form of Shale,

due to intimate association of the oxides, the burnability is improved. Besides impurities in the raw materials reduce the q value of the lattice.

Uniformity of raw mix and the intimacy of the contact between particles lower the diffusion path and hence, increases diffusion rate. Under isothermic conditions, the layer of reaction product increases according to the formula (49),

$$y^2 = 2K \Theta$$

where   k   =   constant depending on the mobility and the diffusion factors in the system,

         Θ =   Time of the reaction.

The composition of the raw feed probably has the most important effect. Because it not only determines the lowest temperature at which the liquid phase will first be formed, but also determines the amount of liquid that will be formed at any temperature. Besides it will also determine the nature of the crystalline compounds that will be formed, and the rates of such formations, as established by the mass law. This is called the Compound Saturation Effect.

At the burning zone of the kiln, the diffusion rate as determined by the amount of the liquid phase formed, has a profound effect on the rate kinetics.

From the phase equilibria data we learn that in a mixture of CaO, Al_2O_3 , Fe_2O_3 and SiO_2, in proportions found in portland cement, where only C_3S , C_2S, C_3A and C_4AF are formed, the first melting irrespective of our choice of starting

mineral always occurs at 1338°C. The composition of this first liquid formed is always the same. It contain 54.8% CaO, 22.7% Al_2O_3, 16.5% Fe_2O_3 and 6% SiO_2 or 1.4% C_3S, 16.2% C_2S, 32.3% C_3A and 50.2% C_4AF. So the ratio of C_4AF: C_3A is 1.56:1.

As more heat is delivered, the temperature remains constant until all liquid of this composition, that can form, has been produced. As long as the compounds which this liquid can contain are potentially available in the mixture, they will keep entering the liquid state with the heat input. So the amount of the liquid that can be formed during clinkering, at any given temperature, is limited by the compound, which will first disappear from the mixture as a potential crystalline phase. This is why sometimes C_3A acts as a flux (as found by Koyanagi (50)); some times C_4AF acts as a flux (as found by Blank (51)); and some times C_2S acts as a flux (as found by Dahl (52)).

Suppose in the mixture of C_3S, C_2S, C_3A and C_4AF; C_4AF is very low. Then naturally C_4AF acts as a flux limiting the amount of the liquid formed. The amount of liquid formed will go on increasing as we increase C_4AF content until we reach the ratio of C_4AF: C_3A = 1.56 : 1. In this case any change in the quantity of other compounds cannot change the amount of the liquid formed, though it may change the percentage of the liquid formed.

Bogue and Taylor (53) reported that the maximum fluxing action occured when C_4AF: C_3A ratio was between 1.5 and 2.0.

Temperature is also an important parameter affecting the reaction kinetics because it determines the mobility of the reacting species during the diffusion process. But then the temperature should not be raised too high, otherwise free CaO grains forming out of the dissociation of calcium silicates and aluminates, grow so much in size and becomes such large in quantity, that later on as a result of it, they cannot recombine to form C_3S and C_3A once again, during the cooling process. This is referred to as "overburning."

2.14 EFFECT OF COMPOUND SATURATION AND THE ROLE OF THE MINERALIZERS:

Within definite limits, introduction of some new components to the $CaO-Al_2O_3-SiO_2$ system, in the region of portland cement composition range, lowers the temperature of the liquid formation. This is precisely the role of a mineralizer which essentially acts as a fluxing agent. But whether that will lead to improved burnability, that is, whether it will make the removal of free CaO more easy, depends on the composition of the initial mixture. And this effect is due to the compound saturation.

Finally, in the end, lime is removed through the following reaction,

$$CaO + C_2S --- C_3S$$
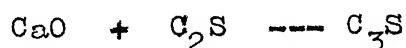
Rate of this reaction would be determined both by the Mass Law as well as the amount of the liquid formed. Just having formed more liquid, and thereby having increased the diffusion rate, through a deliberate use of a mineralizer will not

succed to increase the rate of the above reaction if the
Mass Law does not encourage the formation of C_3S.

For example, a portland cement mix containing 66%
CaO, 11% Al_2O_3 and 23% SiO_2, has a high proportion of C_2S
at clinkering temperature. Now When Fe_2O_3 is used as a flux,
it lowers the first liquid formation temperature by reacting
with C_3A to form C_4AF. Through this reaction, not only a
liquid is being formed and difffusion rate is being made to
increase, but also excess CaO is being released to react
with already excess of C_2 S present and this forces the
equilibrium to move more in favour of C_3S production. This
excess CaO is released by the reaction because tribasic C_3A
is being changed into dibasic C_4 AF.

On the other hand, take another example of portland
cement mix containing 70% CaO, 11% Al_2O_3 and 19% SiO_2. This
will have very little C_2S at the clinkering temperature. Now
when Fe_2O_3 is used as a flux here, again both the liquid phase
and the excess CaO are formed. This excess CaO now cannot
react with C_2S to form C_3S because hardly any C_2S is available
and equilibrium constant at a given temperature is fixed. So
the burnability goes down and the very purpose of using a
flux is defeated because a larg quantity of free lime has
been left behind. The liquid formation, to a certain extent,
only moderates downthe rate at which the burnability falls.

So the concept of compound saturation shows how the
character of the reaction involved with the formation of the
liquid phase is also important in determining the kinetics of
the reaction.

Now we come to the role played by the specific mineralizers. Studies of a wide range of mineralizers, as a fluxing agent, have been made in the USSR in various papers (54-56). Following mineralizers have been used as a fluxing agent;

1. Fluorspar or Calcium Fluoride
2. Calcium Phosphate.
3. Boric Acid
4. Cryolite
5. Magnesium Oxide
6. Magnesium Fluosilicate
7. Sodium Fluosilicate..
8. Calcium Fluosilicate.

We now discuss them one at a time.

2.14.1 Calcium fluoride (CaF_2)

When added 1 to 3%, the temperature of initial liquid formation is reduced by several hundred degrees and the clinkering temperature is reduced by 50 to 100°C. This increases the combination of lime. But then it forms a solid solution with C_3S which gives a lower strength than pure C_3S.

Again C_3A does not form in the presence of CaF_2 and it is replaced by $C_{12}A_7$ making some additional lime available for the formation of C_3S. This will be useful only in mixes having a high proportion of C_2S. Even in this case, the net effect of CaF_2 is determined by the balance between the increase in C_3S formation and the decrease in its cementing properties.

Difficulties with setting time, a reduction in early strength, and increased dusting of the clinker have also occured in some cases. CaF_2 is said to increase $\gamma''- C_2S$ content at the expense of the $\beta-$ form.

Eitel reported (57) that though CaF_2 promoted formation of C_3S, yet presence of CaF_2 accelerated the decomposition of C_3S below 1250°C. So when CaF_2 is used, it is advisable to cool the clinker as rapidly as possible to a temperature below 1250°C.

The presence of CaF_2 also causes the rapid deterioration of the refactory lining of the kiln. But then it has been claimedby Konovalev and Skue (58) that an addition of 0.5%, in the dry mix, forms a stable coating, though not with appreciably higher or lower contents.

2.14.2 Calcium phosphate ($Ca_3 (PO_4)_2$)

It was not found to be very effective. Its presence, many a time, increased the free CaO content. Phosphates are known to decompose C_3S forming a series of solid solution between C_2S and $3CaO. P_2O_5$. Nurse reported (59) that for each 1% P_2O_5 added to a cement mix the C_3S is lowered by 9.9% and the C_2S (now in a solid solution) raised by 10.9%. With increasing amount of phosphate the phosphatic dicalcium silicate phase can be stabilized in turn in the β, α' and α-forms. When so stabilized with phosphate, the α-form has no cementing

properties and the α' very little, but the β-form has good cementing properties.

Besides Calcium phosphate plays no role in reducing the C_2S inversion. As per I.S. Specification 269-1976, P_2O_5 cannot exceed 2.25% in ordinary portland cements as already mentioned in section 2.2.

2.14.3 Boric Acid (H_3BO_3)

It completely prevents the $\beta - \gamma$ inversion of the C_2S, but it was not found effective in promoting the combination of CaO. In fact, in some experiments, the addition of B_2O_3 resulted in an increased amount of free CaO in the clinkers.

2.14.4 Cryolite ($Na_3 AlF_6$)

It was found to be some what more effective than calcium fluoride. The white portland cement industry uses this as a fluxing agent. It was found to reduce the uncombined CaO in all mixtures, but then had the disadvantage of slightly increasing the $\gamma - C_2S$ at the expense of the $\beta -$ form.

2.14.5 Magnesium Oxide (MgO)

In ternary system $CaO-Al_2O_3- SiO_2$ the liquid at the clinkering temperature is deficient in lime and in order to maintain equilibrium during the cooling it has to desolve some solid C_3S and deposit out C_2S Conversely in the system $CaO- Al_2O_3 - Fe_2O_3$ the corresponding liquid contains an excess of lime and has to dissolve

C_2S crystals and deposit out C_3S. In the quaternary system $CaO-Al_2O_3 - SiO_2 - Fe_2O_3$, either conditions can arise depending on the Al_2O_3/Fe_2O_3 ratio. In practice the cooling reaction occurs only partially at best because the equilibrium is frozen. So the position of the C_3S primary phase field, at the clinkering temperature, in a particular system is of great importance, because it determines the relative amounts of C_3S and C_2S present at the clinkering temperature.

Introduction of 5% Mgo into mixes of CaO, Al_2O_3, SiO_2, Fe_2O_3, cause a slight displacement of C_3S primary phase field towards more acidic regions. By favouring a more basic solid and more acidic liquid, it raises slightly the amount of C_3S present at the clinkering temperature. For a frozen equilibrium it means more of C_3S.

Magnesium oxide plays the above role in addition to its role as a fluxing agent. When added to a $C_3S- C_2S- C_3A$ mix it lowers the minimum eutectic melting temperature by 80°C. As a flux, Mgo can never play a negative role due to the effects of compound saturation, because presence of MgO always increases the C_2S content at equilibrium.

The Mgo content cannot exceed 6% in ordinary portland cement as per the I.S. Specification 269-1976, because the presence of crystals of periclase (MgO) leads to a long term unsoundness in the resultant cement because of the expansion that accompanies its slow

no such undesirable effects. Again smaller the size of the periclase crystals less is the hazard. because they hydrate fast enough.

2.14.6   Magnesium Fluosilicate $(MgSiF_6)$

When introduced as the hexa-hydrate, it shows outstandingly superior qualities, both in respect to an improved combination and to a diminished C_2S inversion. In mixtures of composition 2.5 CaO: 1 SiO_2 the free CaO was reduced to about one tenth of its value in the corresponding untreated samples, and in mixtures of composition 3 CaO: 1 SiO_2, to about one fifth. Even at temperatures below those of the lowest melting point (i.e 1455°C in the $CaO-Al_2O_3-SiO_2$ system), the presence of the magnesium fluosilicate produced nearly complete combination.

Flint (60) points out that $MgSiF_6$ loses SiF_4 on ignition which is immediately available for entering into as exchange equilibrium with the SiO_4 -groups, thereby activating them and facilitating their combination with CaO. And once $MgSiF_6$ loses SiF_4 there is left a residue of MgF_2 , which like CaF_2 , is once again active in a similar way, i.e., formation of SiF_4- groups entering into an exchange equilibrium with the SiO_4 -groups.

2.14.7   Sodium and Calcium Silico fluorides
    ($NaSiF_6$ and $CaSiF_6$)

Some work has been done on these in USSR(61). Little literature is available. Sodium fluosilicate has been reported to be better than calcium fluosilicate.

2.15 HEAT TREATMENT OF CLINKERS:

The rate at which the cement clinker is cooled and the proportion of the clinker liquid which is forzen to a glass has a significant effect on the properties of the resultant cement. It affects the grindability, setting time, development of early strength, heat of hydration, drying shrinkage, soundness, resistance against sulphate action and the colour. Close control of the cooling rate is not normally exercised and it is not surprising therefore to find that the glass content varies over a wide range. Values from 2 to 21% have been found by Leroh (62) for commercial clinkers. However the majority of the commercial clinkers show glass contents between 2 and 12% though, some or all of this glass may actually be a very fine textured devitrification product.

In the laboratory tests increasing glass content have been found to make clinker rather less easy to grind, but in commercial manufacture it has sometimes been found that air quenching has a favourable influence on grinding. This apparently variable behaviour may perhaps be explained by the observation made by Ackman and Keil (63), that the matrix of cement clinker is made more difficult to grind by rapid cooling from the burning temperature to 1250°C, but that silicates become more easily ground.

The setting time is not influenced in any consistent manner by the proportion of glass, except that, completely crystalline clinker containing more than 10% C_3A tends to have a flash set.

The rate of cooling, within the limits practicable commercially, seems to have no very significant effect on the strength upto 7 days, but fast cooling rates tend to increase the strength somewhat at 28 days. Very slow cooling, such as is only practicable in the laboratory, reduces the strength at all ages. This is associated with the tendency to dust and the conversion of the calcium ortho-silicate to the γ-form. In quickly or intermediately cooled clinkers, layers of glass are formed aroung the grains of β-C_2S and so the more physical pressure created on the crystal grains blocks the the inversion wave which has to necessarily progress with a large volume expension. This hypothesis was forwarded by Dyckerhoff (64) and by Hansen and Bogeue (65).

There is little evidence that the drying shrinkage may be lower in a glassy than crystalline cements. Available data are inadequate to support any general conclusion, though initially it was held that more glass means less drying shrinkage.

The heat of hydration, as would be expected, increases with the glass content, for the same cement composition. No significant effect has been found at early ages, but at 7 and 28 days a consistent increase has been found with the increasing glass content.

Most important effect of the rate of cooling of a clinker is on the soundness of the resultant cement and its resistance to the action of sulphate solutions. The crystals of MgO, due to slow hydration process, leads to a slow expension resulting in a long term unsoundness in the resultant

cement. This effect is more pronounced when the size of the crystals are large. The liquid present during the burning of clinker can dissolve about 5% MgO which is equivalent to 1.5 to 2% on the total cement composition. So larger contents of MgO can therefore, be tolerated in clinkers that are rapidly cooled because fast cooling leads to a larger quantity of glass formation and prevents the grain growth.

The resistance of portland cement to attack by sulphate solutions is known to be related in a general way to their calculated C_3A content, but there are many anomalies in this relationship. One explanation is to be found in Parker's observation (66), that sulphate resistance is much increased by rapid cooling and that when the aluminate is present in the glass, it is much less susceptible to attack by sodium or magnesium sulphate.

To a large extent the colour of ordinary portland cement depends on whether the iron containing liquid freezes to a glass or crystallizes as C_4AF. Reddish, yellowish or brownish colour emerges as a result of iron containing liquid freezing to form glass. We have more pleasing colours, like dark blue, if we allow at least a part of iron to crystallize as C_4AF or a solid solution of Mgo and C_4AF.

2.16 CLINKER GRINDING:

The hot clinkers coming out of the rotary kilns contains around 296 to 300 KCals. of heat per kg. After being cooled in enclosed air circulating cooler, a carefully adjusted amount of retarder consisting of gypsum ($CaSO_4$. $2H_2O$) or

plaster of paris ($CaSO_4 . 1/2 H_2O$) are added in order to prevent too rapid a setting time. The amount of gypsum required to produce the most favourable time - of - set has been found to depend largely on the alumina content of the mixture.

Hansen and Hunt (67) have reported that 25% to 75% of the gypsum could be replaced with natural anhydrite without adversely affecting either the setting times or the strength or the volume change characteristics of the concrete made from them. The effect of talc as an impurity in the gypsum has been examined by Yamane and Toyama (68). They reported that the addition of 1% talc increased the grinding efficiency by about 6%, and it had little effect on setting time or heat stability but then it reduced the compressive and flexural strengths by about 14% and 4% respectively.

Along with the retarder, other approved materials like grinding aid, colouring agent, surfactants and air-entraining agents may be admixed with the clinker upto 1% by mass. All these are then ground till the specific surface area exceeds 2250 cm^2./gm. as per I.S. Specification; 269-1976.

If the cement is too coarse, segregation or 'bleeding' may occur, and the water will not be able to react with it rapidly enough to develop the greater value in the cement.

As reported by Swenson and Flint (69), C_2S tends to be more concentrated in the coarser fraction of the cement (40 to + 55 microns) while the C_3S tends to be more concentrated in the finer fraction (0 to 22 microns). Of the other phases,

there is a little consistent variation except that the $CaSO_4$ is contained almost entirely in the 0-22 micron fraction. As the grain size of the cement increases the heat of hydration is found to decrease regularly at all ages.

There is some difference of opinion with respect to finer grinding, but it is usually maintained that the cement will develop its strength the more rapidly, the finer it is ground, but that very quality may deprive the cement of a reserve of hydratable materials which may be of a great value.

2.17 STORAGE OF CEMENT:

The ground cement is usually stored in concrete silos and then packed in gunny bags, 50 Kgs. to the bag, for shipment.

Storage of cement in the bins has been reported not to be harmful, but on the contrary to be possibly beneficial. If small amounts of lime have remained uncombined during the burning, the product may be slightly unsound. But on storing for a brief period, this lime hydrates and carbonates by reacting with the moist air, thereby becoming incapable of causing unsoundness.

Prolonged storage in gunny bags, under conditions where moist air may gain access to the cement, has been found to result in a decrease in strength of the test specimens, especially at early ages. Under such conditions, a partial hydration takes place, as a result of which the ignition loss is increased. The cement appears to be coarser to the touch, the amount of water required to make up a neat cement paste of standard consistency increases and the setting time is

CHAPTER # III

SYNTHESIS OF WHITE PORTLAND CEMENT
FROM RICE HUSK ASH

In the present work white portland cement had been
synthesised under 46 different conditions of fluxing
agents, temperature of firing, time of holding, mor-
phology of raw materials, and heat treatment of the
clinkers. This chapter deals with the raw materials,
their preparation and characterization as done in the
laboratory. It deals with the design of the cement
mix. Then it deals with the synthesis of the cements.
Finally a catalogue of all the cements, which were
systhesised is given.

3.1 RAW MATERIALS USED:

Portland cement is manufactured from a proportioned
mixed containing silica, lime, alumina, suitable fluxing
agents, moisture and some gang materials. The fluxing
agents or the gang materials should not introduce excess of
the deleterious compounds mentioned in the section 2.2. Nor
should they, for the production of white portland cement,
introduce any colour imparting constituent. Most of the
colour imparting constituent come in along with the gang
materials accompanying the alumino-silicates in the raw
materials. So for the production of white portland cement
one has to either purify the alumino-silicates or one has
to use pure sources of silica and alumina. In the present
work we chose the second option.

In our work the raw materials used are,

1. Rice Husk Ash - as a pure source of silica.

2. Hydrated lime - as a source of lime.

3. Bayer's alumina - as a pure source of alumina.

As a fluxing agent, the following were used one at a time,

1. Magnesium oxide.

2. Boric acid.

3. Calcium fluoride.

4. Calcium phosphate.

5. Sodium Silico-fluoride.

Now each of the raw materials are dealt with separately below.

3.1.1. Rice husk ash:

Rice husk ash is obtained by incinerating rice husk. Rice husk (also called hulls) consists of the outer shell covering the rice kernel. Rice husk is a by-product produced in the milling of paddy and forms 16-25% by weight of the paddy processed. The chaff obtained during the winnowing on the farm, mainly consists of unmature paddy without any kernel, which could also be considered as a kind of rice husk. Chaff probably constitutes at least 3% of the paddy produced. Going by the 1980 data, about seventeen million tonnes of rice husk and 2.5 millions tonnes of chaff are produced annually in India.

The rice husk obtained from small sized village mills and the huller-type mills usually contains about 65% husk, 30% bran, 5% polish and small amount of broken grains. This is used mostly as a cattle feed. Rice husk produced in the bigger mills, especially in the Eastern

India, is mostly used as a fuel in the rice parboiling units.

Rice husk contains about 72% by weight organic matter. For preliminary calculations, however the following average values, on % dry weight basis may be considered representative:

Table # 3.1

Ash	-	20%
Lignin	-	22%
Cellulose	-	38%
Pentosans	-	18%
Other organic matter like - crude protein, crude fat, etc.		2%

Moisture content may be considered to be 9% (on wet basis), corresponding to a relative humidity of about 50%. These representative values may, however, vary widely. These values probably depend on the type of paddy, degree of husk contamination, the geo-cultural conditions and methods of analysis. For more details, one may refer to the paper presented by Govindarao (70).

The ash is the inorganic component of the rice husk. Depending on the temperature of incineration, the ash is either in the crystabolite and trydymite form or in the reactive amorphous form. A typical composition of the ash, by wt.% is given in the next page.

Table # 3.2

SiO_2	—	95%
K_2O	—	1%
CaO	—	1%
P_2O_5	—	2%
(Na_2O_3		
(Fe_2O_3	—	1%
(MgO		

So ash is a very pure source of silica. It is cheap too. Today it costs Re. 0.50 per 40 Kgs. bag.

3.1.2   Hydrated Lime:

Hydrated lime is made from the quicklime (calcium oxide). Quicklime is made industrially by heating limestone, obtained from the lime quarries, in the vertical or rotary kilns at 800° - 1000°C. It comes in the form of white or brownish white hard stratified thick plates or irregular blocks.

At Kanpur, quicklime comes from both Katni and Satna. Katni lime is considered superior. It is more than 95% pure and costs around Rs. 550/- per tonne.

Slaked lime is prepared by sprincling calculated quantity of water over the quicklime.

3.1.3   Bayer's alumina:

Alumina, (Al_2O_3) occurs naturally in the form of bauxite, corundum, ruby, emerald, topaz, sapphire and amethyst. Presence of the impurities

Bauxite is an important mineral because aluminium metal is extracted from it through electrolysis in molten cryolite. Before electrolysis, bauxite is purified through the Bayer's process and hence the name Bayer's alumina.

In the Bayer's process powdered bauxite is dissolved in hot concentrated sodium hydroxide solution under pressure when sodium aluminate solution forms:

$$2 \ NaOH + Al_2O_3 = 2Na \ AlO_2 + H_2O$$
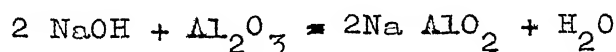
Iron oxide, titanium dioxide and most of the silicates present do not dissolve in the alkali and are filtered off as a sludge. The filtrate is diluted and seeded with aluminium hydroxide crystals and stirred for several days, when hydrolysis of the aluminate occurs thus:

$$Na \ AlO_2 + 2H_2O = Al(OH)_3 + NaOH$$
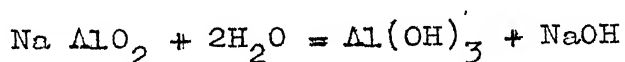
The precipitated hydroxide is filtered off, washed, dried and heated strongly to the pure oxide known as Bayer's alumina, whilst the sodium hydroxide solution is concentrated and used again.

Bayer's alumina is a sparkling white, hard, crystalline powder, around 98% pure, - 100 mesh ASTM in size and costs around Rs. 500/- per tonne.

3.1.4 Fluxes:

Excepting for the Boric acid - all the other fluxes used were of a commercial grade and were assumed

to be 95% pure. Boric acid was a G.R. Grade laboratory regent, 99.5%. All the fluxes used were in a powdered state and excepting for calcium fluoride and magnesium oxide, were sparkling white in colour. Calcium fluoride had a dirty yellowish tinge and magnesium oxide had a light bluish gray tinge.

3.2 PREPARATION OF THE PRINCIPAL RAW MATERIALS:

White rice husk ash had been prepared from the rice husk. Whiteness was emphasised because we did not know what role the carbon or organic matter might play during the clinkerization. Black activated carbon might be left trapped during the clinkerization and later it might impart a gray colour to the ground cement. Again trapped carbon is known to hinder the setting of cements. Besides presence of carbon or organic matter might increase the interparticle distance and hence by increasing the diffusion path it might lower the reaction kinetics. So through the controlled incineration process whitest possible ash had to be prepared.

Slaked lime had to be prepared from around 95% pure quicklime blocks because it gives highly reactive lime. Again it is much easier to blend slaked lime with other raw materials, because it will not pick up moisture during the blending operation. With slaked lime it is easier to ball-up the raw feed.

Ash and slaked lime were both highly reactive, and so in order to facilitate both the blending of the raw materials, as well as sintering and clinkerization, the Bayer's alumina had

The exact steps which were taken to prepare the raw materials in the laboratory are now given below in detail.

3.2.1 Rice Husk Ash Making:

Rice husk has a low calorific value and a low efficiency of burning. It cannot burn and give a flame like the other fuels. Only about half of the heat potential in rice husk represent the volatilizable level and the rest of it exist in the fixed carbon portion. (71). The calorific value of rice husk is 2,900 to 3,400 Kcal./kg. as reported by Maheshwari and Ojha (72).

Burning is relatively easier when the husk is in the state of suspension. Otherwise due to incomplete combustion, the ash is contaminated with carbon. Reported designs of most furnaces for the combustion of rice husk incorporate this feature (73). So we have either jet-type furnaces or fluidized bed reactors.

But for our purpose, in the laboratory we tried to get white ash by the controlled incineration process. We tried to control the volume of air in take during the incineration as well as the degree of heat loses. We even externally heated the rice husk ash using 1000 watt heating element rods. We designed and fabricated two mild steel furnaces having a 40 Kgs. capacity each.

The first furnace was more primitive in design. The schematic diagram of this furnace is given in page No. 69. The husk was kept in a cylindrical wire-mesh

Outermost M.S. Sheath

Rice husk

Wire mesh bask

Wire mesh Chim

M.S. Stand

SCALE 1:
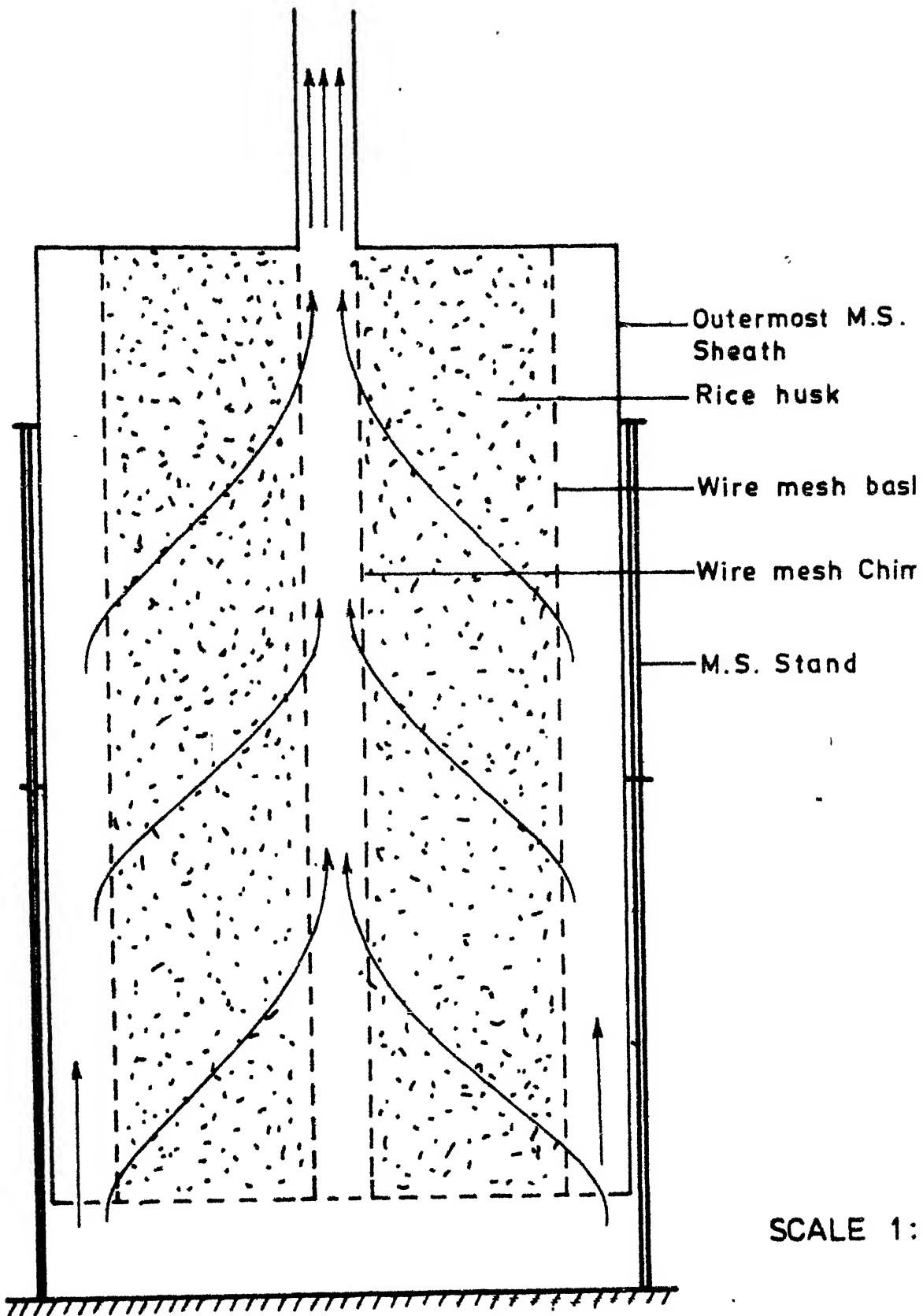
Fig. 3.1 Furnace No. 1 (40 Kg Capacity)

basket having a diameter of 38.5 cms. and a height of 80 cms. At the centre of the basket, a wire-mesh tubular chimney was concentrically fitted along the axis. The chimney had a diameter of 5 cm. and height of 100 cms. The husk was kept in the annular space between the chimney and the wire-mesh basket. The set-up of the basket containing rice husk and the chimney was concentrically placed within a mild steel tubular outer covering, having trapping for holding the basket. This outer most tubular sheeth made out of sheet metal had a diameter of 48.5 cms. and a height of 80 cms. and was placed 8 cms. above the ground using a tripod stand made of the mild steel rods. This clear space below the furnace set-up, allowed air to rush in from the underneath and circulate in the annular space between the basket and the outer-most sheet metal sheath. The furnace was closed from the top using a lid. However, at the centre of that lid, there was a circular opening of 5 cms. diameter for the chimney to pop out by 20 cms. So after entering the annular space of 5 cms. clearance between the basket and the outer-most sheath the air had no way to escape. So it had to travel through the burning rice husk and then escape through the open chimney. The draft produced by the rising column of hot gases in the chimney was sufficient to pull the air through the husk.

As the burning operation proceeded, as the husk changed into ash, the volume decreased. This created sufficient gap at the upper end of the basket,

thus providing an easy path for the air to escape. The burning operation took full 48 hours and the ash produced was light gray in colour.

The defects which were apparent in the first furnace were rectified in the second furnace which naturally then turned out to be quite sophisticated. In the second furnace the wire-mesh used for the basket and the tubular chimney was replaced by perforated Mild steel sheet metal. This made the basket more sturdy and it made it possible for the rice husk to be rammed in. This lowered the volume change on burning. Then the top 20 cms. of the perforated basket was covered with clayey mud film on the outside. This insured that, at the later stages no air could enter the top 20 cms. of the empty basket from the sides and hence find an easy path of escape directly into the chimney.

Now in order to control the inflow of air more effectively from underneath the furnace, we raised the furnace, above the ground level, by 16 cms. instead of 8 cms. and covered the bottom with a sheet metal having a 4 cms. long tubular opening with a flap valve inside it. This valve was made out of a circular sheet metal. When kept horizontally it did not allow any air to enter the tubular opening because the diameter of the sheet metal valve was same as that of the tubular opening. With a lever projecting outside, this flap could slowly be turned from the horizontal to the vertical position, thereby

Clay Coverered Chimney

Clay Covered

Perforated Shee
Metal Chimney

Perforated Shee
Metal Basket

Outer Jacket

Rice Husk

Electric Heatin
Rod

M.S. Stand

M.S. Sheath

Glass Wool

Flap for regula
air inflow

SCALE 1:5
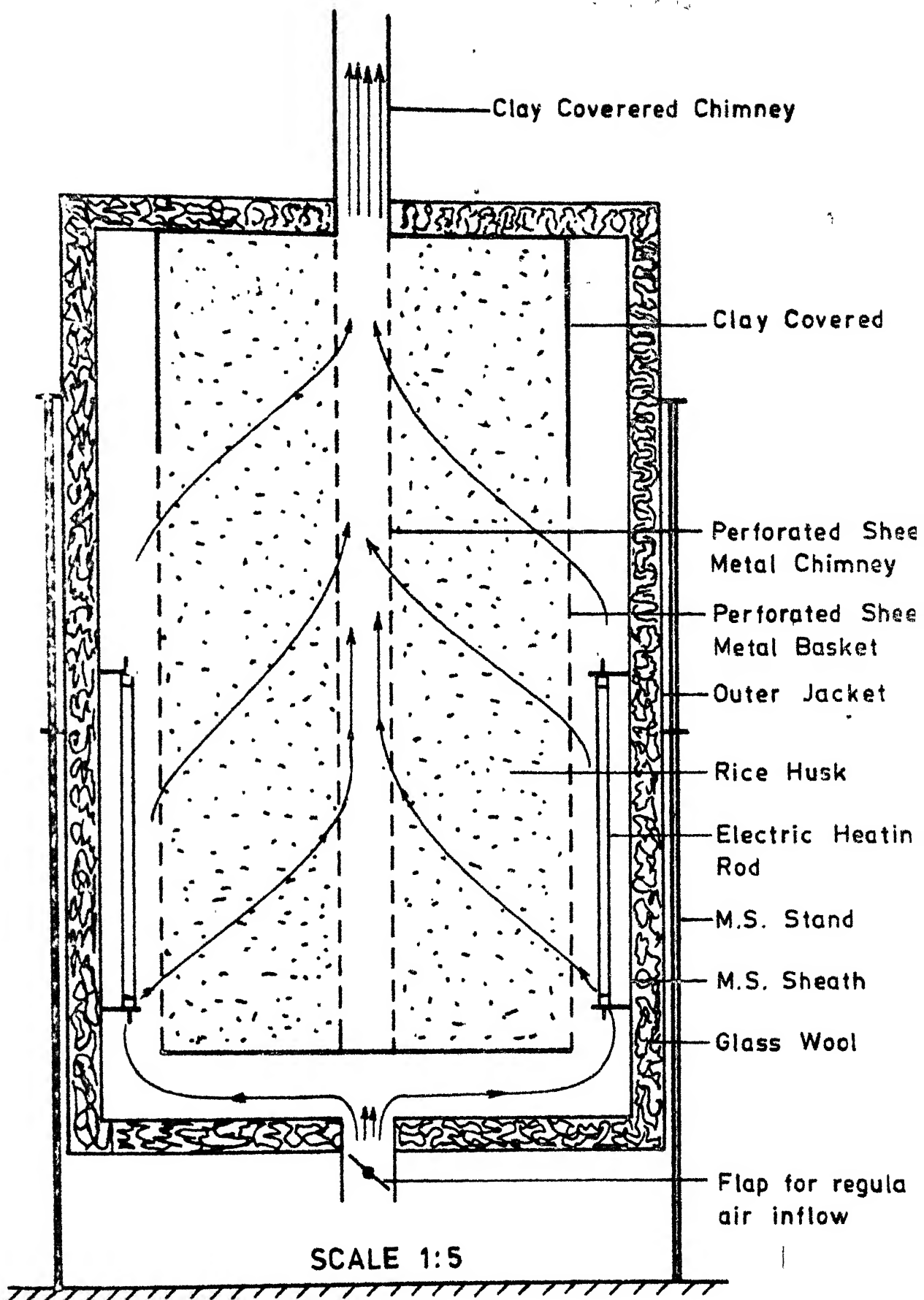
This control mechanism was necessary because specially towards the end of the burning operation excess air flowing in through the ash had the effect of cooling it down.

Again in order to increase the duration of low temperature smouldering of the ash, and in order to thereby facilitate the removal of carbonaceous materials the outer most sheet metal sheath was provided with a jacket on the outer side. Between the sheath and the jacket there was an annular space with 3 cms. clearance and this space was packed in with glass wool. Even the top covering lid had a 3 cms. thick glass wood placed on it similarly with a jacket. And in the annular space of 5 cms. clearance between the basket and the sheath, 6 heating element rods of 1000 watts each were operated electrically. These heating rods were switched on towards the end of the burning operation.

The second burning operation continued over a period of 72 hours. The total process was through a subdued smoldering. No flames were made with kerosene and the smoldering proceeded from the top to the bottom. The ash produced was mostly white in colour. There were still pockets of black ash at the base plate of the basket because air could not enter that region. After grinding the white ash alongwith an ash having a light gray tinge, below -200 mesh ASTM size, it became light gray in colour. This ash was used for cement making, hoping that the coluur

would vanish during firing at high temperature. And it did.

The schematic diagram of this modified furnace is given in page No. 72.

3.2.2. Hydrated Lime Making:

Chunks of quicklime obtained from the Katni lime quarries was first tested for the percentage of calcium in accordance with the I.S. Specification: 4285 - 1967 and was found to be 94.74% pure. Now 1 kg. of pure calcium oxide requires 321.25 gms. of water. So Katni quicklime required theoretically 305.19 gms. of water. But in practice a part of this water is lost through steaming. So excess water is taken. It is sprinkled slowly over quicklime chunks. Quicklime crumbles to a powder. Sprinkling is done with constant agitation of the powder with a glass rod. Finally the fine hydrated power is sieved out.

In a typical example 366 gms. of water was sprinkled over 1140 gms. of quicklime. Later on more water was sprinkled in order to componsate for the amount lost through steaming. The the powder was sieved out using a sieve No. 20 (having an opening of 840 microns). As a result 1166 gms. of hydrated lime was separated from the bits of unreacted quicklime. So 800 gms. of quicklime reacted with 366 gms. of water, when it should have required only 257 gms. of water. So every 100 gms. of hydrated lime contain 3.98 gms. of impurities and 10.31 gms. of excess water. So purity level of the hydrated lime was 87.5% in this particular batch. This infact

3.2.3 Activated alumina making:

Since hydrated lime and rice husk ash was being used in a ultrafine powder form, it was necessary to use -200 mesh ASTM size activated Bayer's alumina.

So 341 gms. of -100 mesh ASTM size Bayer's alumina was ground in a ceramic ball-mill using 1320 gms. of 87 ceramic cylpeps of assorted size for 18 hours. It yielded 367 gms. of activated alumina of -200 mesh ASTM size . The excess of 26 gms. of material probably came from the cylpeps and jar themselves. The purity level of the activated alumina was taken to be 98%.

3.3 CHARACTERIZATION OF RICE HUSK AND RICE HUSK ASH:

Rice husk ash being a new raw material for portland cement manufacture a detailed characterization is necessary.

In the unground state, the rice husk is greyish brown, tough, woody and abrasive. It has high proportion of crude fibre. It shows good resistance to weathering and occupies volumetrically about 8 times the space required for paddy of equal weight. The unground husk has paddy length varying from 2 to 4 times its width and has a bulk density of about 0.1 gm./cc. The true density of husk is 0.75 gms./cc. It can be readily compressed to about 0.5 gms./cc. Grinding to various degrees of fineness increases the bulk density 2 to 5 times. These characteristics have an important bearing on the transportation and storage of rice husk.

Rice husk ash, when made by incinerating the unground husk, has the same shape and form of the husk. But it easily crumbles to a fine powder of light gray colour. It is abrasive and highly friable. The bulk density of the ash is 0.1 to 0.2 gms./cc. The size distribution of the unground black as well as white ash is given below in table nos. 3.3 and 3.4. Ash of -200mesh ASTM size can easily be produced by grinding it in a ball-mill for barely 20 minutes.

TABLE NO. 3.3

SIEVING ANALYSIS OF BLACK RICE HUSK ASH

1. Weight of the Sample = 67.5 gms.

2. Sieving time = 10 minutes.

Sl. No.	Ash Size	Weight in gms.	% of total wt.
1.	+ 14 mesh ASTM	1.25	1.85
2.	-14 + 20 mesh ASTM	2.20	3.26
3.	-20 + 28 mesh ASTM	3.50	5.19
4.	-28 + 48 mesh ASTM	12.25	18.15
5.	-48 + 60 mesh ASTM	9.75	14.44
6.	-60 +100 mesh ASTM	8.00	11.85
7.	-100 mesh ASTM	33.00	48.89

TABLE NO. 3.4

SIEVING ANALYSIS OF WHITE RICE HUSK ASH

1. Weight of the Sample = 300 gms.
2. Sieving time = 10 minutes.

Sl.No.	Ash Size	Weight in gms.	% of total wt.
1.	+ 14 mesh ASTM	1.70	0.57
2.	−14 + 20 mesh ASTM	2.50	0.83
3.	−20 + 28 mesh ASTM	10.00	3.33
4.	−28 + 48 mesh ASTM	60.20	20.07
5.	−28 + 65 mesh ASTM	44.20	14.73
6.	−65 +100 mesh ASTM	34.25	11.42
7.	−100 mesh ASTM	148.00	49.33

3.4 DESIGN OF THE CEMENT MIX:

A typical oxide composition of the raw feed for ordinary portland cement type 1 is as follows:

TABLE NO. 3.5

wt.% SiO_2	=	21.3
wt.% CaO	=	63.2
wt.% Al_2O_3	=	6.0
wt.% Fe_2O_3	=	2.7

wt.% MgO	–	2.9
wt.% SO$_3$	–	1.8
wt.% Insoluble	–	0.2
wt.% Loss	–	1.3
		99.4

For white portland cement, the raw feed oxide composition is going to vary slightly because there, the percentage of impurities and Fe_2O_3 is lower. Percentage of Al_2O_3 cannot be made to go up otherwise there will be a flash-set. Therefore percentage SiO_2 and CaO has to increase. In-fact a typical oxide composition of raw feed for white portland cement is given below:

TABLE NO. 3.6

wt.% SiO$_2$	–	25.5
wt.% CaO	–	65.0
wt.% Al$_2$O$_3$	–	5.9
wt.% Fe$_2$O$_3$,FeO	–	0.6
wt.% MgO	–	1.1
wt.% SO$_3$	–	0.1
		98.2

For the above two oxide compositions, the potential for the formation of the cementing phases is given below in Table No. 3.7. These potential have been calculated as per Lee and Parker's equation given in page no. 36

TABLE # 3.7

	For oxide composition given in Table # 3.5	For oxide composition given in Table # 3.6
wt.% C_3S	51.27	30.35
wt.% C_2S	22.39	50.20
wt.% C_3A	11.33	14.62
wt.% C_4AF	8.22	1.83

Because in the white portland cement raw mix, the proportionate increase in the SiO_2 is greater than the increase in the CaO, the C_3S potential has decreased while the C_2S potential has increased significantly. On top of it, the ratio of C_3S/C_2S is much lower in practice than that indicated by the potential. This can be seen from the following table which gives the percentage of the phases actually formed for the portland cement oxide composition given in table number 3.5.

TABLE # 3.8

wt.% C_3S	—	45.0
wt.% C_2S	—	27.0
wt.% C_3A	—	11.0
wt.% C_4AF	—	8.0
wt.% $CaSO_4$	—	3.1
wt.% MgO	—	2.9
wt.% Free CaO	—	0.5
		97.5

So if we were to adopt the oxide composition given in Table number 3.6, we would be getting very little C_3S and lots of C_2S. As this would mean low initial strength, it is undesirable. So we chose to increase the % CaO in our raw feed to 68.5% and reduce the % SiO_2 to 23.5%, after having first established that 68.5% CaO does not lead to unsoundness owing to the free lime.

As a result, for our white portland cement synthesis the following oxide composition was taken,

Table # 3.9

wt.% SiO_2	—	23.5
wt.% CaO	—	68.5
wt.% Al_2O_3	—	6.0
wt.% Fe_2O_3	—	0.1
wt.% others	—	1.9
		100.0

As it can be seen from the above table **we have only 1.9%** impurity level in the oxide composition. This is inspite of the fact that the rice husk ash and the activated alumina have been assumed to be 94% and 98% pure respectively and the hydrated lime has been found to be around 83.64 to 87.5% pure. This happens because the 1.9% impurity level shown in Table no. 3.9 is residual impurity. Most of the actual **impurities** in the raw materials are either in the form of carbon, moisture or other volatizable constituents.

Given the oxide composition in Table no. 3.9,
as per the Lea and Parker's equation given in page no. 36 ,
the potential for the various cementing phases will be as
shown below:

Table # 3.10

wt.% C_3S	–	59.84
wt.% C_2S	–	22.22
wt.% C_3A	–	15.73
wt.% C_4AF	–	0.30
		98.09

This proportion for the potential of the cementing phases
is quite satisfactory.

Whenever any flux is used, it is done at the
expense of CaO. The purity level of most of the fluxes
has been assumed to be 95% and only 2 wt.% of flux has been
used. This lowered the weight % of CaO to 66.5. This naturally
will change the proportion of the potential phases a bit , as
can be seen from the Table given below:

Table # 3.11

wt.% C_3S	–	51.70
wt.% C_2S	–	28.37
wt.% C_3A	–	15.73
wt.% C_4AF	–	0.30
		96.1

So even with the presence of 2 wt.% flux, the proportion for the potential of the various cementing phases remains satisfactory.

The oxide composition given in Table no. 3.9 also satisfies the first stipulation laid down in IS Specification; 269-1976, under the heading of Chemical requirements, because

$$\frac{wt.\%\ CaO - o.7\ wt.\%\ SO_3}{2.8\ wt.\%\ SiO_2 + 1.2\ wt.\%\ Al_2O_3 + 0.65\ wt.\%\ Fe_2O_3} = 0.938.$$

3.5 PROCESS FOR THE WHITE PORTLAND CEMENT SYNTHESIS:

The first step is to prepare 225 gms. of oxide raw feed containing rice husk ash, hydrated lime, activated Bayer's alumina and flux, in such a way that the oxides are present in the proportion given in Table No. 3.9. For 225 gms. mix we take 56.25 gms. of rice husk ash, 225.92 gms. of 87.5% pure hydrated lime, 13.78 gms. of activated alumina and 4.74 gms. of flux. The total weight of the raw feed becomes 300.69 gms. This is then blended in a tray for at-least 5 minutes. Then it is put in a 6 inch ceramic ball-mill containing 1320 gms. of 87 ceramic cylpeps of assorted size and ground for 2 hours.

The ground raw feed is collected in a tray, after separating the grinding media, and then it is kneaded into a plastic mass with sufficient water for 10 minutes. This plastic mass is then balled up into balls of around 4 to 5 cms. diameter. These are then dried in the oven at about 80°C for 24 hours in order to remove all free moisture. These dried

balls are white hard masses weighing around 33.5 gms. when the diameter is 4 cms.

These dried balls are then kept inside the globular furnace in silliminite crucible and then fired at various temperatures for various duration of time. After firing, the loss in weight varies from 19.72% to 20.49%. The globular furnace used had 6 silicon carbide rods as heating elements. Typical heating cycles of the furnace is given in page no.84. After firing the clinkers are either cooled inside the furnace, or cooled in the air or cooled with the help of a table fan. The fan cools the surface of the clinker from 1350°C to about room temperature within 4 minutes.

Some of the clinkers were found to be very friable while some others were quite hard. There were interesting colour variations at the surface at times.

All these clinkers were separately ground in a ceramic ball-mill containing 1320 gms. of 87 ceramic cylpops of assorted size for 2 hours, before being packed in the polythene bags.

3.6 CATALOGUE OF VARIOUS WHITE PORTLAND CEMENTS SYNTHESISED:

A large number of white portland cements have been synthesised in the present work. They were tested for various properties and as a result a vast amount of data was generated. In order to make the presentation concise and unwieldy, the results have been reported against a cement number assigned to each sample of cement. In order to render a meaning to these cement numbers, the catalogue given below was devised.
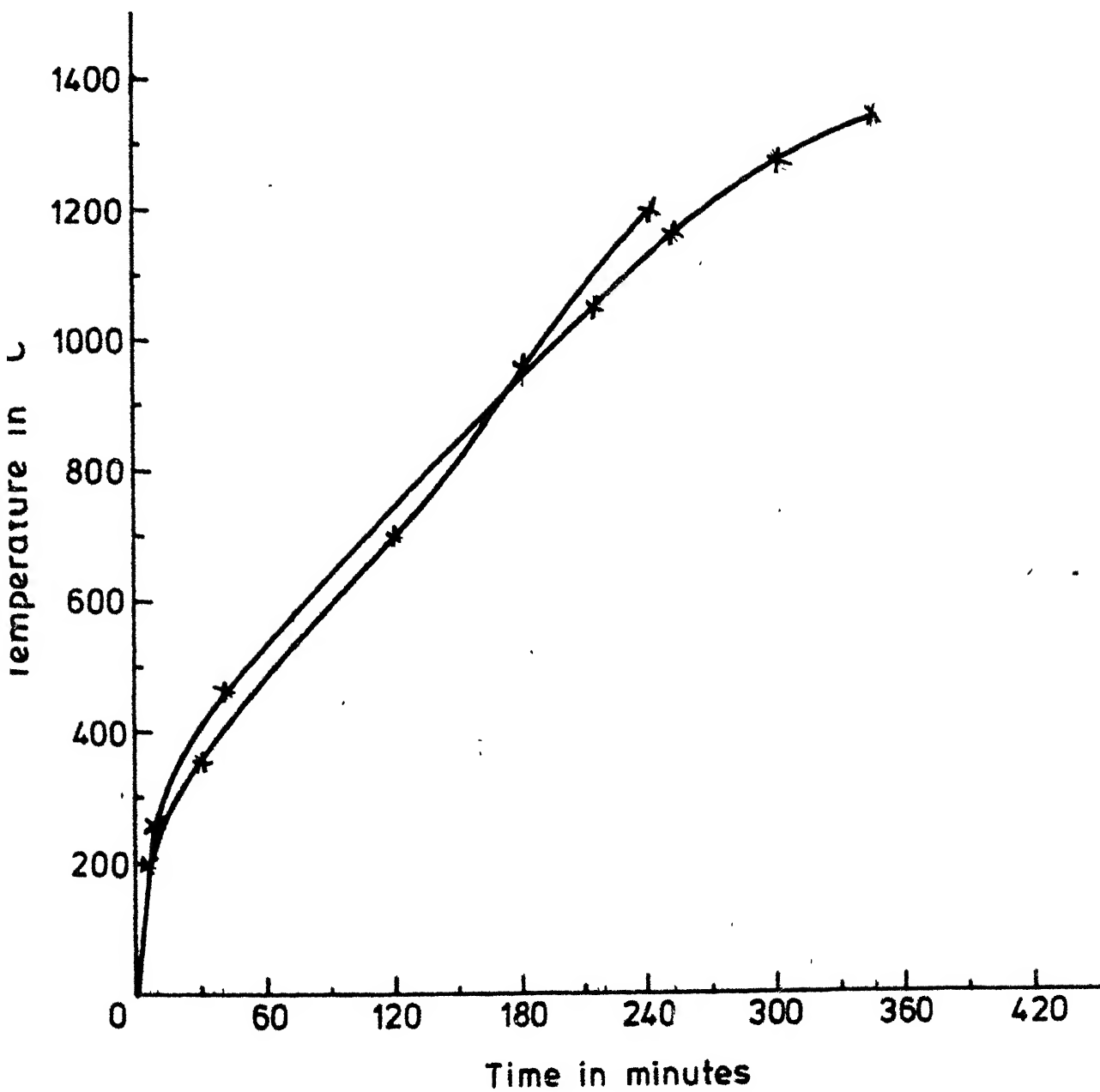
Fig. 3.3 Heating cycle of the furnace.

This catalogue gives the composition; morphology and the purity level of the raw materials; firing temperature; soaking time and heat treatment of clinkers against each cement number.

TABLE # 3.12

CATALOGUE OF THE CEMENTS

Cement No.	Composition /Morphology	Firing Temp./ Soaking time.	Heat treatment of clinkers.
C-1	62% CaO; GR grade laboratory reagent, 99% pure; 25% SiO_2, RHA, 94% pure; 8% Al_2O_3 , chromatographic grade, 99% pure; 5% MgO, commercial grade 95% pure.	1350°C 30 mins.	Fan cooled.
C-2	-do-	1350°C 161 mins.	-do-
C-3	-do-	1375°C 30 mins.	-do-
C-4	68.5% CaO, GR grade laboratory reagent, 99% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 0% flux.	1350°C 1 hour.	Air cooled.
C-5	-do-	-do-	Fan cooled.
C-6	-do-	-do-	Furnace cooled.

C-7	63.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 5% MgO, commercial grade, 95% pure.	1. 1350°C 1 hour.	Air cooled.
C-8	-do-	-do-	Fan cooled.
C-9	-do-	-do-	Furnace cooled.
C-10	66.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% MgO, commercial grade, 95% pure.	-do-	Air cooled.
C-11	-do-	-do-	Fan cooled.
C-12	-do-	-do-	Furnace cooled.
C-13	66.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% Boric acid, GR grade laboratory reagent, 99.5% pure.	-do-	Air cooled.
C-14	-do-	-do-	Fan cooled.
C-15	-do-	-do-	Furnace cooled.

C-16	66.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO$_2$, RHA, 94% pure; 6% activated Bayer's Al$_2$O$_3$, 98% pure; 2% Sodium fluosilicate, commercial grade, 95% pure.	1350°C. 1 hour. But this sample had been heated to 1200°-1300°C once before.	Air cooled.
C-17	—do—	1350°C. 1 hour.	—do—
C-18	—do—	—do—	Fan cooled.
C-19	—do—	—do—	Furnace cooled.
C-20	68.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO$_2$, RHA, 94% pure; 6% activated Bayer's Al$_2$O$_3$, 98% pure; 0% flux.	—do—	Fan cooled.
C-21	66.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO$_2$, RHA, 94% pure; 6% activated Bayer's Al$_2$O$_3$, 98% pure; 2% Calcium fluoride, commercial grade, 95% pure.	—do—	Air cooled.
C-22	—do—	—do—	Fan cooled.
C-23	—do—	—do—	Furnace cooled.

C-24	66.5% CaO, hydrated lime commercial grade, 81.125% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% Calcium phosphate, commercial grade, 95% pure.	1350°C 1 hour.	Air cooled.
C-25	—do—	—do—	Fan cooled.
C-26	—do—	—do—	Furnace cooled.
C-27	68.5% CaO, hydrated lime Katni grade, 87.5% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 0% : flux.	1200°C 2 hrs.	Air cooled.
C-28	—do—	1200°C 4 hrs.	—do—
C-29	—do—	1200°C 6 hrs.	—do—
C-30	66.5% CaO, hydrated lime Katni grade, 87.5% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% Sodium Fluosilicate, commercial grade, 95% pure.	1200°C 4 hrs.	—do—
C-31	—do—	1200°C 10 hrs.	Furnace cooled.
C-32	—do—	1150°C 5 hrs.	Air cooled.
C-33	—do—	1150°C 7 hrs.	—do—

C-34	66.5% CaO, hydrated lime Katni grade, 87.5% pure; 23.5% SiO_2, RHA, 94% pure;. 6% activated Bayer's Al_2O_3, 98% pure; 2% Sodium Fluosilicate, commercial grade, 95% pure.	1150°C 7 hrs.	Furnace cooled.
C-35	-do-	1100°C 5 hrs.	Air cooled.
C-36	-do-	1100°C 7 hrs.	-do-
C-37	-do-	1100°C 9 hrs.	-do-
C-38	66.5% CaO, hydrated lime Katni grade, 87.27% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% Sodium Fluosilicate, commercial grade, 95% pure.	1050°C 5 hrs.	-do-
C-39	-do-	1050°C 7 hrs.	-do-
C-40	-do-	1050°C 9 hrs.	-do-
C-41	-do-	1000°C 5 hrs.	-do-
C-42	-do-	1000°C 7 hrs.	-do-
C-43	-do-	1000°C 9 hrs.	-do-

C-44	66.5% CaO, hydrated lime Katni grade, 87.27% pure; 23.5% SiO_2, RHA, 94% pure; 6% unactified, + 200 mesh ASTM, Bayer's Al_2O_3, 98% pure. 2% Sodium Fluosilicate, commercial grade, 95% pure.	1200°C 4 hrs.	Air cooled.
C-45	66.5% CaO, hydrated lime Katni grade, 87.27% pure; 23.5% SiO_2, Jet Black RHA, 30.5% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% Sodium Fluosilicate, commercial grade, 95% pure.	-do-	-do-
C-46	66.5% CaO, hydrated lime Katni grade, 83.64% pure; 23.5% SiO_2, RHA, 94% pure; 6% activated Bayer's Al_2O_3, 98% pure; 2% Sodium Fluosilicate, commercial grade, 95% pure.	-do-	Furnaced cooled.

C-47 White portland cement manufactured by the Associated Cement Company Limited.

EVALUATION OF CEMENTS

Cement samples were X-ray analysed, and tested for their strength, colour, tap density, friability and workability. This chapter explains the significance of these tests. Then it discusses the procedures and the limitation of these tests.

4.1 SIGNIFICANCE OF THE VARIOUS TESTS CONDUCTED:

Testing of portland cement is a highly evolved branch in itself. We have an I.S. Specification: 4031-1968, on "Methods of Physical Tests for Hydraulic Cement" and another I.S. Specification: 4032-1968, on "Method of Chemical Analysis of Hydraulic Cement." Due to lack of time these specifications could not be followed most of the time, nor could most of the tests mentioned be carried out.

Strength is the most primary characteristic of any cement and hence its study is obvious. Since the present work concerned white portland cement alone, the study of colour was essential. Various fluxes used, could have imparted colour or a tint to the cement. Besides, the degree of whiteness varies over a wide range and its exact determination was necessary.

Detailed X-ray analysis of the raw materials, A.C.C. white portland cement and most of the synthesised cement samples was done in order to get a quantitative estimate of the various phases present to the first order of approximation. This data is expected to theoretically substantiate the strength

values obtained for the various cements. It also gives a deeper insight into the process of clinkerization. The raw materials were analysed for prominent peaks. These peaks were then studied in the cement samples, and the extant to which they were found to have diminished was indicative of the degree to which the clinkerization process had progressed. Presence of free lime is also easily indicated by the X-ray analysis.

Lower tap density means greater volume of mortar for the same weight of cement and hence the same price. Since it directly effects the economy it is an important parameter for study. Greater friability of clinker means lasser cost of grinding. This also effect the economy directly. Better workability means more areas of application and this also indirectly helps the economy.

4.2   PROCEDURE OF STRENGTH ANALYSIS:

For studying the 3- and 7- day strength character-istics of the various cement samples, tensile strength analysis of neat cement cylindrical pellets were done, based on the Brazillean Technique, because with this mode of testing it was possible to make a large number of samples using less cement. Later cold crushing test was conducted on 16 cement-sand mortar cubes.

For the tensile strength analysis, neat cement pastes were made with water/cement ratio of 1:3 each time. Using stainless steel mold, cylindrical pellets were made out of these pastes. The pellets had a diameter of around 10 mm,

height of around 10 mm and the weight of the dried pellets were around 1.30 gms. These pellets were kept in air for 4½ to 8 hours before being immersed in water. When dropped in water, a violent stream of air bubbles emerged out of these pellets, with a loud distinct hissing sound and this continued for about 30 minutes. It was probably due to the water rushing into the pellets through the fine capillaries. The force produced by the emerging air bubbles was enough, at times, to break up a 5hours - old pellet. These pellets were cured in water for 3 and 7 days. Then after accurately measuring their diameter and height, they were broken under the calibrated Instron machine, model TT-CM-L .

While breaking, these pellets were kept horizontally along the axis on their curved cylindrical surface. A cold compressive load was then applied along two straight lines on the curved cylindrical surface, with a cross-head speed of 0.5 mm/min. The load cell had a capacity of 5000 Kgs. The stress-strain curve was plotted on a chart moving at the rate of 20 mm/min. The crack propagated vertically downwards, along a surface, splitting the pellet into 2 halves, through a tensile force distributed across the cracked surface.

The 7 day old pellets made out of cement no. 31, was so hard that it was very difficult to break it into 2 halves. The periphery peeled off progressively through slip mechanism, leaving the hard core intact.

The tensile strength of the pellets were found from the relation given in the next page,

$$\text{Tensile strength in Kgf./cm}^2 = \frac{0.636 \quad \text{Load to fracture in Kgs.}}{\text{Diameter in cms. x Height in cms.}}$$

The compressive strength of cement is generally 8 to 9 times the tensile strength.

For molding these pellets, Plaster of Paris mold, wood mold, aluminium mold, perspecs mold and stainless steel mole were used one at a time. The stainless steel mold was found to be best suited for the job. With Plaster of Paris mold, due to the $CaSO_4$ pick-up, the setting time was adversely affected.

For cold crushing test, 5 cms. x 5 cms. x 5 cms. cement-sand mortar cubes were made using cement nos. 46 and 47. Ordinary Ganga sand was used after thoroughly washing it 8 times in order to remove the clay and the mica, as they are known to interfere adversely with the setting of cement. In the first 8 cubes, the cement/sand ratio was 1:3 and water/cement ratio was 1.7692 by weight. A dry cube with A.C.C. cement weighed 223.5 grms. while that with cement no. 46 weighed 213.3 gms. In the next 8 cubes, while the cement/sand ratio remained the same, the water/cement ratio was changed to 1:2 by weight.

These cubes were made using hand pressure, in the Steel molds, manufactured by Associated Instrument Manufacturers, as per the I.S. Specification: 4031-1968. These cubes were cured in air for 1 day and then they were further cured under water for 2 and 6 days. The cured cubes were then cold crushed with a cross-head speed of 0.5 mm/min. and the cold compressive

strength was then measured through a stress-strain plot on a chart moving at the rate of 20 mm/min. For the first 8 cubes Instron machine, Model 1195 was used while for the last 8 cubes Instron machine, Model TT-CM-L was used. The cracks first developed from along the top side edges, moving down, in a concave inwards fashion. Later these cracks moved downwords from along the top side edges along a surface inclined at -45° to the horizontal plane.

4.3   LIMITATIONS OF THE STRENGTH ANALYSIS:

For the tensile strength analysis of the pellets, there were only two minor sources of error. First the pellets being green, weak and plastic at the time of being ejected out of the molds, at times, their shapes got slightly distorted. At times the curved surface was not truly cylindrical or the flat end surfaces were not truly parallel. The second error was due to the fact that some times minute blow hole, due to the trapped air bubbles were distributed inside the pellets. Though the volume of the blow holes was negligible, they still tend to reduce the strength.

For the cube testing, the only possible source of error arose due to the occasional surface blemishes. This was a negligible source of error.

4.4   PROCEDURE OF THE X-RAY ANALYSIS:

Minus 200 mesh ASTM cement samples were X-ray analysed on a Seifert X-ray machine, Model No. ISO-DEBYEFLEX 2002.

At least 22 phases are present in a cement sample, producing 584 peaks amongst them. This makes the X-ray analysis very difficult, because it is not easy to resolve a desired peak, with perfect clarity, from this cluster. Off the 22 phases, only the following 16 have been studied. The figures within the paranthesis indicate the number of peaks associated with the respective phases.

1. CaO (13)
2. $CaCO_3$ (43)
3. SiO_2 (26)
4. $-Al_2O_3$ (37)
5. $-Al_2O_3$ (27)
6. $-Al_2O_3$ (14)
7. $KC_{23}S_{12}$ (15)
8. NC_8A_3 (27)
9. C_3S (22)
10. $-C_2S$ (11)
11. $-C_2S$ (30)
12. $-C_2S$ (33)
13. C_3A (54)
14. C_5A_3 (51)
15. C_2F (19)
16. C_4AF (29)

A quantitative estimation, to the first order of approximation, was made for the above mentioned phases by studying the peak height, at 2 safe d-values, for each of these phases. By safe d-values, we mean those, at which the desired peaks are not only sharp, strong, but also free of the interfering peaks belonging to the other phases. Yet for some phases like $KC_{23}S_{12}$ or NC_8A_3 it was not possible to find two such d-values. While for some the peaks were found to be mixed with the back-ground and they have been referred to as 'BM'. The following safe d-values, were found for each of the phase under study. The corresponding 2θ values when Chromium target is used with K_{β_1} radiation, is also given in

TABLE # 4.1

S.No.	Phase	d-value in $\AA$	2θ values (valid only for $K\alpha_1$ radiation from the Chromium target)
1.	CaO	2.405	56.8880°
		2.778	48.7047°
2.	$CaCO_3$	3.035	44.3492°
		2.095	66.2926°
3.	SiO_2	1.815	78.2670°
		1.378	112.4604°
4.	$\alpha-Al_2O_3$	3.479	38.4480°
		1.601	91.3668°
5.	$\beta-Al_2O_3$	2.820	47.9334°
		2.420	56.5036°
6.	$\gamma-Al_2O_3$	2.450	55.7510°
		1.388	111.2356°
7.	$KC_{23}S_{12}$	1.959	71.5690°
8.	NC_8A_3	1.558	94.6546°
9.	C_3S	3.020	44.5812°
		2.178	63.4634°
10.	$\alpha-C_2S$	2.700	50.2076°
		2.810	48.1148°
11.	$\beta-C_2S$	2.780	48.6674°
		2.182	63.3334°
12.	$\gamma-C_2S$	2.740	49.4250°
		3.000	44.8946°

13.	C_3A	1.554	94.9752°
		1.204	144.1324°
14.	C_5A_3	2.670	50.8116°
		2.980	45.2126°
15.	C_2F	1.940	72.3800°
		1.840	77.0058°
16.	C_4AF	2.630	51.6408°
		1.572	93.5534°

In order to reduce the possibility of mutual masking between the closely clustered peaks, very slow scanning rate of 0.6°/minute and a low time constant of 3 seconds were adopted. So the resolution was of the order of 0.03° on the 2θ scale. The chart speed was fixed at 30 mm/minute so that the resolution along the chart was 1.5 mm. The counts/second was kept at 100. Using Chromium target, the Kα_1 radiation having a wavelength of 2.291002 Å was employed through a monochromator. Receiving slit width was 0.3 mm and the scanning slit width was 2 mm. These parameters were held constant through out the X-ray analysis of the various samples.

Due to error in the mechanical alignment of the X-ray diffraction goniometer, a lateral shift of the peaks was observed along the horizontal axis. This shift varied from 3.02 mm to 4.845 mm. Using G.R. Grade known laboratory reagents

peak obtained from a 100% pure phase. Since it is difficult to procure 100% pure cementing phases we could not find the exact quantitative value of the phases present in absolute terms. We only made a comparative study of the amount of phases present with respect to the amount of similar phases present in pure A.C.C. white portland cement by comparing the peak height.

Some of the 584 d-values are very closely spaced and even a low time constant of 3 seconds is not enough for good resolution because the mechanical response time of the stylus is too sluggish.

Yet another source of error creeps in due to the defective 2θ degree marking of the stylus. During the course of the present work it was not exactly 50 mm. apart always. In one case, the error in the stylus marking was of the order of 3 mm. Again the lateral shift of the peaks along the horizontal axis, due to the mechanical mis-alignment of the X-ray diffraction goniometer, was not independent of the scanning angle. At one instance, the $CaCO_3$ peak pertaining to the d-value of 3.035 $\overset{o}{A}$ was shifted by 3.6 mm while that pertaining to the d-value of 2.095 $\overset{o}{A}$ was shifted by 5.45 mm. But when incorporating a correction factor only an average value was taken. A similar limitation applied to the back-ground noise correction factor.

In order to ensure that the X-ray data do not become meaningless, one has to employ a good judgement based on a long experience, during the analysis of the X-ray data.

4.6   PROCEDURE OF THE COLOUR ANALYSIS:

People with normal vision see every thing in colour. Their eyes perceive the light scattered from the surfaces of objects as colours, all of which diverge from pure white. The art of colour abstraction was born from the time of Ice Age man who could distinguish colours as existing independently of the objects.

American research has found as many as 10 million colour variations between the neutral whites, grays and blacks, and all the different chromatic colours (73). In order to enable us to 'think in colour' a colour name is developed which is so characteristic of the colour's appearance that it is readily understood by others. All names should correspond to specific colours or colour areas, and the areas they designate should not unduly overlap. Because a colour cannot be whiter than white, blacker than black, and because its strength or intensity cannot increase beyound a certain limit, we can only have a finite number of names with a specific meaning. Approximately 8000 colour names are registered in the U.S. alone, and the possibility of forming new neames is almost unlimited (73).

A colour is supposed to have a Hue, Saturation, Shade, Lightness, Warmth, and a Value. Hue is that attribute of a colour which determines its name in every day speech. Human eye can distinguish 4 primary hues: yellow, red, blue and green. At one and the same time, in any given colour, the sensation of yelloness and blueness or the sensation redness

and greenness cannot be experienced. Yellow-blue or red-green combinations give rise to irreconcilable perceptions. But any one colour from one of these group can mix well with any other colour in the any other group. For example, yellow and red can be perceived simultaneously as two components in orange, or red and blue can be perceived simultaneously as two components in violet. A continuous variation of one primary hue in another in all possible combination constitutes what is known as 'colour circle'. Now a colour can have a single or double or a multiple hue content. When creating a colour with a double hue content, following facts should be kept in mind, and this will be necessary if annihilation of cement colours are called for.

1. When we just begin to add one hue to a colour with some other colour with a single hue content, it can be likened to a fork in a road that has turned off in a new direction. Colours lying close to this fork seem to vie for dominance and are difficult to combine without creating an unstable, disturbing visual appearance. In a double hue content colour, eight such forks are possible where the primaries undergo decisive changes in hue.

2. The father the hues lie from each other in the colour circle, greater is their mutual reinforcement. This reciprocal action may produce a pleasing impression in some instances, but the combination of 2 very potent hues will result in discordant, flickering

3. Colours which lie within the same range between two
   pure hues, in colour circle will combine well, but
   a combination of colours from different ranges --
   such as the yellow-red and blue-red ranges--- may
   produce unpleasant tensions.

The dynamics of colour involving a subtle balance between
hues do not admit to analysis according to absolute rules and
this makes things difficult.

The term 'Saturation' refers to colour density or
intensity. Any colour is perceived as immersed in neutral
white of varying strength. Saturation indicates inversely
the extent of the neutral white component in any colour. Higher
the saturation more distinct is the hue. The effect of
saturation is so strong that for a given hue with varying
saturation, the family resemblance is less pronounced. Increa-
sing saturation reduces lively colours to bare tints.

'Shade' also known as shadow, is the amount of black
which is present in a colour or is the amount of reduced light
in a particular area. With increasing shade the colour becomes
deeper. The family resemblance between colours is most
evident when shading is the only variable. Gray is just
shaded white. The shade determines the tone of a colour. The
shade scale is produced by addition of increasingly deep
shadows to a particular hue.

The lightness or the darkness of a colour is
related to the extent of the visible spectrum contained in
that colour. Yellows are light as they include most of the

spectrum, while reds are dark as they include only one extreme of the spectrum. Different hues of the same intensity may vary in lightness. In Munsell Book of Colour, however, to indicate the degree of lightness or darkness the term 'Value' has been used. This should not be confused with our term 'Value' which has been used here in accordance with the artist's use of the French word 'Valeur'.

The so-called cool colours, like green, blue and violet are those which can tolerate even the deepest shading without apparent hue changes. We accordingly do not assign special names to their shaded versions. The warm colours, like yellow and red, on the other hand, are profoundly affected by shading. Darkening yellow results in a green shift. This shift is primarily psychological.

The 'Value' of a colour, also known as its distinctness or clarity refers to that special appearance which arises out of the combined effect of saturation and shading present in varying degrees. Since hue is the most obvious characteristic of colour, we tend to attribute any discord between 2 colours to differences in hue. The real cause of discord may, however, often be traced to differences in value.

Now as far as determination of the colour of our cement samples is concerned, we used the Reinhold Colour Atlas edited by A. Kornerup and J.H. Wanscher and published by Reinhold Publishing Corporation, New York.

Reinhold Colour Atlas contains 1266 colour swatches systematically organized. There are 30 hues with 8 saturation

levels for each hue and 6 shade levels for each saturation.
The colour plates or swatches are printed with printing inks
obtained from Sadolin and Holmblad Ltd.; Copenhagen. First
the inks or blends of the inks were used to print the basic
colour of each plate on special white paper, producing
unshaded, 100% saturated colour. Saturation was varied by
etching the plate to form a fine network of elevated dots and
surrounding depressions. The size of the dots determined the
saturation value. The shading was provided by repeated
application of transparent gray inks over these colour plates.
With every additional application of transparent gray ink, the
shade became one degree deeper.

In order to find the colour of the cement samples, a
small   amount of cement had to be placed in the folded part
of a gray finder so that only a small square of the colour is
visible through the opening. Then we turn to the colour plate
that most closely resembles the colour of the sample. Trial
and error method is employed. When the closest swatch is
selected, the colour of the sample is identified according to
the plate number, column letter and row number. The plate
number indicate the hue, the column letter indicates the degree
of shade and the row number indicate the degree of saturation.
Then turning to the end of the Atlas, we find the name pertaining
to the colour of the selected swatch.

4.7   LIMITATIONS OF THE COLOUR ANALYSIS:

While selecting the correct swatch or colour plate
one has to be very careful because there are several ways for

the error to crop in. When colours are to be compared they have to be brought close together without any marked line of differentiation between them, like, a gap. If there is a space between them, the observer is obliged to relcy to some degree on his colour memory, which will weaken his discriminatory powers. The longer the period of time that elapses between his perception of each of the two colours, the more dependent he will be on his memory. Most people have poorly developed colour memory.

Besides the two colours to be compared should lie flat on surface since only a very slight difference in their position in relation to the source of light will cause one to seem slightly more shaded than the other. Again as a rule, colours attain their true appearance in good daylight or in light from a window that does not face the Sun and is therefore, not golden in tone. Reflections from a painted wall can influence the appearance of colour to a great degree.

Light should be allowed to striked the colour plate at a 45° angle while regarding the plate at a 90° angle. This avoids reflection from the glossy surface of the paper.

4.8 PROCEDURE AND LIMITATIONS FOR TAPDENSITY, FRIABILITY AND WORKABILITY ANALYSIS OF CEMENTS:

Tap density of the cement sample was found out by collecting a small amount of cement in a 10 ml. graduated measuring cylinder and then after tapping it 6 times it was weighed on the electronic weighing machine, Model: Sartorious/ 1216 MP. From the weight obtained the weight of the empty measuring cylinder was subtracted. The net weight of cement is then

divided by the volume of the cement as seen from the measuring cylinder to give the tap density in grams/cc.

Since the error in the volume measurement is only of the order of 0.1 cc, and that in weight of the order of 0.1 gms., the tap density obtained is quite accurate.

The friability of the clinker was only qualitatively gauged by pressing cold cement clinkers with fingers. The workability was also qualitatively gauged while making the neat cement pellets and the cement - sand mortar cubes.

RESULTS AND DISCUSSION

In this chapter, the results are first reported in the following order -- strength analysis, X-ray analysis, tap density, colour analysis, friability and workability. The effects of the various para- meters are then discussed in detail.

5.1 RESULTS:

TABLE # 5.1.1

3 - DAYS ± 1 HOUR CURED TENSILE STRENGTH OF NEAT CEMENT SPECIMENS

(Cross-head speed = 0.5 mm/minute)

ment No.	Diameter in cms.	Height in cms.	Fracture load in kgf.	Tensile strength (T.S.)in Kgf./cm^2	Average T.S. in Kgf./cm^2	Standard deviat- ion.	Average T.S.as % of ACC white portland cement.
1	2	3	4	5	6	7	8
C-1	1.105	1.169	30.0	14.77	10.68	2.92	-65.02%
	1.153	1.213	20.0	9.10			
	1.200	1.169	18.0	8.16			
C-2	1.118	1.115	42.0	21.43	17.95	2.79	-41.22%
	1.173	1.152	31.0	14.59			
	1.161	1.168	38.0	17.82			
C-3	1.201	1.155	26.0	11.92	14.63	3.01	-52.07%
	1.113	1.217	28.0	13.15			
	1.178	1.147	40.0	18.83			
C-4	1.111	1.123	21.2	10.81	8.69	1.89	-71.55%
	1.115	1.126	17.8	9.02			
	1.127	1.141	12.6	6.23			

1	2	3	4	5	6	7	8
C-5	1.200	1.169	22.0	9.97	9.30	0.51	-69.55%
	1.200	1.182	20.5	9.19			
	1.201	1.153	19.0	8.73			
C-6	1.112	1.133	14.4	7.27	7.65	2.06	-74.94%
	1.127	1.113	20.4	10.34			
	1.146	1.123	10.8	5.34			
C-7	1.130	1.124	22.0	11.02	11.43	0.61	-62.56%
	1.145	1.214	24.0	10.98			
	1.169	1.151	26.0	12.29			
C-8	1.216	1.224	24.0	10.26	10.94	0.92	-64.18%
	1.209	1.173	23.0	10.32			
	1.212	1.244	29.0	12.23			
C-9	1.116	1.015	20.8	11.68	11.58	0.32	-62.08%
	1.110	1.131	22.0	11.15			
	1.113	1.119	23.3	11.90			
C-10	1.010	1.017	19.0	11.76	13.52	1.29	-55.73%
	1.009	1.015	22.5	13.97			
	1.030	1.017	24.0	14.82			
C-11	1.022	1.010	22.4	13.80	14.76	0.78	-51.65%
	1.013	1.020	24.0	14.77			
	1.009	1.027	25.6	15.71			
C-12	1.007	1.040	20.0	12.15	12.27	0.44	-59.82%
	1.009	1.030	21.0	12.85			
	1.005	1.019	19.0	11.80			

1	2	3	4	5	6	7	8
C-13	1.200	1.238	43.0	18.41	17.60	0.90	-42.35%
	1.197	1.222	41.5	18.04			
	1.209	1.158	36.0	16.35			
C-14	1.211	1.188	42.0	18.57	17.93	1.64	-41.26%
	1.195	1.205	35.5	15.68			
	1.201	1.219	45.0	19.55			
C-15	1.208	1.216	23.0	9.96	12.13	1.67	-60.26%
	1.198	1.153	27.0	12.43			
	1.182	1.191	31.0	14.01			
C-16	1.207	1.236	148.0	63.10	61.65	4.72	+101.93%
	1.200	1.234	155.0	66.57			
	1.211	1.216	128.0	55.28			
C-17	1.015	1.023	54.0	33.08	28.04	3.85	- 8.16%
	1.019	1.025	39.0	23.75			
	1.023	1.025	45.0	27.29			
C-18	1.019	1.019	83.5	51.14	53.04	3.46	+73.73%
	1.019	1.028	82.5	50.09			
	1.021	1.033	96.0	57.89			
C-19	1.006	1.032	30.4	18.62	20.43	1.55	-33.07%
	1.017	1.021	33.1	20.27			
	1.009	1.018	36.2	22.41			
C-20	1.005	1.019	24.0	14.91	11.72	2.73	-61.62%
	1.019	1.015	19.5	11.99			
	1.007	1.033	13.5	8.25			

1	2	3	4	5	6	7	8
C-21	1.005	1.026	21.2	13.08	12.84	0.175	-57.94%
	1.009	1.020	20.5	12.67			
	1.013	1.023	20.8	12.77			
C-22	1.013	1.021	21.0	12.91	14.14	0.97	-53.67%
	1.013	1.028	25.0	15.27			
	1.018	1.030	23.5	14.25			
C-23	1.004	1.003	20.5	12.95	12.5	0.35	-59.06%
	1.007	1.019	19.5	12.09			
	1.009	1.012	20.0	12.46			
C-24	1.018	1.027	42.0	25.55	26.05	1.47	-14.69%
	1.019	1.035	46.5	28.04			
	1.013	1.023	40.0	24.55			
C-25	1.017	1.031	41.5	25.17	28.11	3.49	- 7.92%
	1.015	1.030	43.0	26.16			
	1.014	1.026	54.0	33.01			
C-26	1.007	1.020	33.0	20.43	19.94	0.98	-36.99%
	1.009	1.014	29.0	18.03			
	1.008	1.016	31.0	19.25			
C-27	0.996	1.003	13.0	8.28	8.07	0.62	-73.68%
	1.001	1.010	11.5	7.23			
	1.006	1.018	14.0	8.69			
C-28	1.011	1.032	15.5	9.45	7.43	1.63	-75.67%
	1.010	1.038	9.0	5.46			
	1.012	1.024	12.0	7.57			

1	2	3	4	5	6	7	8
C-29	1.006	1.017	6.0	3.73	3.85	0.15	-87.38%
	1.005	1.012	6.5	4.07			
	1.002	1.014	6.0	3.76			
C-30	1.023	1.029	64.0	38.67	33.92	4.03	+11.10%
	1.018	1.039	57.0	34.27			
	1.123	1.022	52.0	28.82			
C-31	1.019	1.022	11.2	6.84	7.71	0.77	-74.75%
	1.025	1.033	14.5	8.71			
	1.018	1.031	12.5	7.58			
C-32	1.017	1.031	97.0	58.84	52.84	4.90	+73.08%
	1.010	1.035	77.0	46.85			
	1.009	1.032	87.5	52.83			
C-33	1.008	1.012	115.2	71.02	60.49	6.70	+125.35%
	1.004	1.025	120.7	74.60			
	1.007	1.011	94.5	59.04			
C-34	1.016	1.018	76.5	47.04	51.10	4.73	+67.38%
	1.022	1.024	95.0	57.73			
	1.019	1.016	79.0	48.53			
C-35	1.018	1.016	14.5	8.92	9.43	2.37	-69.10%
	1.015	1.008	20.2	12.56			
	1.009	1.017	11.0	6.82			
C-36	1.014	1.040	18.5	11.16	12.30	1.73	-59.71%
	1.011	1.045	24.5	14.75			
	1.013	1.057	18.5	10.99			

1	2	3	4	5	6	7	8
C-37	1.014	1.036	35.0	21.19	19.98	4.26	-34.55%
	1.023	1.046	24.0	14.27			
	1.016	1.048	41.0	24.49			
C-38	1.004	1.008	5.0	3.14	2.94	0.14	-90.37%
	1.001	1.007	4.5	2.84			
	1.001	1.008	4.5	2.84			
C-39	1.000	1.005	4.5	2.85	3.39	0.52	-88.91%
	0.996	0.993	5.0	3.22			
	0.997	1.015	6.5	4.09			
C-40	1.015	1.007	8.0	4.98	4.94	0.13	-83.82%
	0.995	1.006	7.5	4.77			
	1.001	1.002	8.0	5.27			
C-41	1.001	1.004	1.5	0.95	1.24	0.23	-95.94%
	1.008	1.002	2.0	1.26			
	1.003	1.007	2.4	1.51			
C-42	1.043	1.015	3.0	1.80	2.12	0.31	-93.05%
	1.001	1.062	3.4	2.03			
	1.000	1.001	4.0	2.54			
C-43	1.021	1.024	4.5	2.74	2.92	0.34	-90.44
	1.008	1.009	4.2	2.63			
	1.051	1.000	5.6	3.39			
C-44	1.023	1.043	37.0	22.06	23.63	2.65	-22.59%
	1.013	1.044	45.5	27.36			
	1.015	1.050	36.0	21.48			

1	2	3	4	5	6	7	8
C-45	1.008	1.013	51.0	31.77	26.83	4.50	-12.11%
	1.001	1.027	45.0	27.84			
	1.051	1.043	36.0	20.89			
C-46	1.051	1.041	65.0	37.79	35.2	4.03	+15.30%
	1.035	1.043	65.0	38.30			
	1.037	1.039	50.0	29.51			
C-47	1.012	1.033	47.5	28.90	30.53	2.75	+ 0.00%
	1.013	1.032	46.5	28.29			
	1.010	1.042	57.0	34.41			

TABLE # 5.1.2

7 - DAYS ± 2 HOURS CURED TENSILE STRENGTH OF NEAT CEMENT SPECIMENS

(Cross-head speed = 0.5 mm/minute)

ment No.	Diameter in cms.	Height in cms.	Fracture load in kgf.	Tensile strength (T.S.)in Kgf./cm^2	Average TS. in Kgf./cm^2	Standard deviation.	Average T.S. as % of ACC white portland cement.
	2	3	4	5	6	7	8
C-1	1.101	1.027	49.0	27.56	22.64	3.58	-50.80
	1.161	1.139	44.2	21.24			
	1.119	1.153	38.8	19.13			
C-2	1.113	1.117	73.0	37.35	32.61	3.51	-29.14%
	1.187	1.133	66.6	31.50			
	1.141	1.131	58.8	28.98			
C-3	1.151	1.138	55.0	26.71	29.05	3.26	-36.88%
	1.172	1.216	60.0	26.78			
	1.139	1.128	68.0	33.66			
C-4	1.155	1.170	28.0	13.18	10.42	2.30	-77.35%
	1.169	1.126	21.8	10.53			
	1.171	1.149	16.0	7.56			
C-5	1.215	1.162	30.0	13.51	16.19	2.20	-64.81%
	1.211	1.136	35.0	16.18			
	1.208	1.143	41.0	18.89			
C-6	1.133	1.130	11.0	5.46	9.56	3.50	-79.22%
	1.151	1.139	19.0	9.22			
	1.147	1.132	28.6	14.01			

1	2	3	4	5	6	7	8
C-7	1.169	1.200	36.6	16.55	18.18	1.34	-60.50%
	1.170	1.139	38.0	18.14			
	1.141	1.110	39.5	19.84			
C-8	1.215	1.151	53.0	24.10	21.46	1.99	-53.37%
	1.206	1.181	47.0	20.99			
	1.218	1.137	42.0	19.29			
C-9	1.108	1.127	31.5	16.04	16.32	0.94	-64.53%
	1.113	1.007	31.0	17.59			
	1.126	1.112	30.2	15.34			
C-10	1.007	1.038	39.5	24.03	20.29	2.81	-55.92%
	1.008	1.015	31.5	19.58			
	1.008	1.024	28.0	17.25			
C-11	1.031	0.993	32.0	19.88	20.82	1.94	-54.76%
	1.008	1.026	31.0	19.06			
	1.019	1.035	39.0	23.52			
C-12	1.014	1.011	21.0	13.03	15.52	2.02	-66.28%
	1.011	1.013	25.0	15.53			
	1.009	1.016	29.0	17.99			
C-13	1.201	1.216	51.0	22.21	22.50	1.35	-51.12%
	1.200	1.168	53.5	24.28			
	1.213	1.211	48.5	21.00			
C-14	1.213	1.200	53.8	23.51	23.39	1.45	-49.17%
	1.213	1.201	57.5	25.10			
	1.208	1.209	49.5	21.56			

1	2	3	4	5	6	7	8
C-15	1.200	1.200	48.2	21.29	19.79	1.18	-57.00%
	1.205	1.213	45.2	19.67			
	1.209	1.201	42.0	18.40			
C-16	1.204	1.154	180.0	82.39	87.77	3.22	+88.56%
	1.210	1.156	198.0	90.03			
	1.208	1.168	195.0	87.90			
C-17	1.017	1.030	116.5	70.73	73.83	4.78	+60.44%
	1.021	1.025	115.5	70.19			
	1.022	1.031	133.5	80.58			
C-18	1.020	1.025	155.0	91.86	88.82	4.36	+93.01%
	1.020	1.041	138.0	82.66			
	1.021	1.023	151.0	91.95			
C-19	1.027	1.026	84.5	51.00	51.93	0.66	+12.83%
	1.122	1.018	85.5	52.27			
	1.016	1.049	88.0	52.51			
C-20	1.008	0.974	34.0	24.03	20.54	1.07	-55.36%
	1.008	0.968	30.0	19.55			
	1.005	1.026	32.5	20.05			
C-21	1.007	1.015	31.0	19.29	16.46	2.04	-64.23%
	1.013	1.012	25.6	15.51			
	1.001	1.002	23.0	14.58			
C-22	1.012	1.031	29.0	17.68	18.56	1.71	-59.67%
	1.019	1.025	28.0	17.05			
	1.015	1.032	34.5	20.95			

1	2	3	4	5	6	7	8
C-23	1.004	1.005	29.0	18.28	14.49	2.68	-68.51%
	1.003	1.010	20.0	12.56			
	1.010	0.997	20.0	12.63			
C-24	1.016	1.033	59.0	35.75	32.77	2.54	-28.79
	1.010	1.030	54.0	33.01			
	1.013	1.041	49.0	29.55			
C-25	1.010	1.036	53.5	32.52	36.47	3.22	-20.75%
	1.013	1.041	67.0	40.41			
	1.006	1.014	58.5	36.47			
C-26	1.004	1.015	50.5	31.52	32.81	1.42	-28.71%
	1.006	1.033	52.5	32.13			
	1.012	1.030	57.0	34.78			
C-27	0.999	1.001	15.0	9.54	10.76	1.51	-76.62%
	0.999	1.001	15.5	9.86			
	0.980	1.008	20.0	12.88			
C-28	1.006	1.024	20.0	12.37	10.40	1.40	-77.40%
	1.009	1.031	15.0	9.17			
	1.007	1.011	15.5	9.68			
C-29	1.015	1.015	14.0	8.66	8.30	0.56	-81.97%
	0.999	1.021	14.0	8.73			
	1.009	1.009	12.0	7.50			
C-30	1.019	1.027	101.0	61.38	57.21	3.48	+24.32%
	1.020	1.032	87.5	52.87			
	1.017	1.030	94.5	57.38			

1	2	3	4	5	6	7	8
C-31	1.021	1.031	56.0	33.84	34.61	2.47	-24.79%
	1.020	1.035	63.0	37.95			
	1.016	1.016	52.0	32.04			
C-32	1.011	1.013	119.0	73.90	75.20	1.89	+63.40%
	1.010	1.027	127.0	77.87			
	1.003	1.005	117.0	73.82			
C-33	1.015	1.001	361.3	126.32	113.26	11.94	+139.50%
	1.003	1.019	171.5	106.72			
	1.005	1.014	156.6	97.73			
C-34	1.008	1.016	122.0	75.76	82.62	8.20	+79.53%
	1.010	1.030	127.5	77.95			
	1.009	1.031	154.0	94.15			
C-35	1.019	1.020	48.5	29.68	24.98	3.35	-45.71%
	1.017	1.014	37.5	23.13			
	1.016	1.018	36.0	22.14			
C-36	1.015	1.048	46.0	27.50	32.55	3.57	-29.27%
	1.011	1.040	58.0	35.08			
	1.017	1.051	60.0	35.70			
C-37	1.011	1.041	94.0	56.81	64.26	6.99	+39.64%
	1.015	1.013	119.0	73.61			
	1.010	1.030	102.0	62.36			
C-38	0.995	1.009	6.0	3.80	3.77	0.23	-91.81%
	0.998	1.025	6.5	4.04			
	0.996	1.012	5.5	3.47			

1	2	3	4	5	6	7	8
C-39	0.993	0.995	6.0	3.86	4.36	0.73	-90.53%
	0.996	1.000	6.0	3.83			
	1.000	1.005	8.5	5.38			
C-40	0.998	1.012	10.0	6.30	5.84	0.60	-87.32%
	1.001	1.021	10.0	6.22			
	1.000	1.019	8.0	4.99			
C-41	1.001	1.008	3.4	2.14	1.63	0.41	-96.45%
	1.021	1.003	2.6	1.62			
	1.000	1.113	2.0	1.14			
C-42	1.150	1.120	3.8	1.88	2.29	0.44	-95.03%
	1.136	1.133	4.2	2.08			
	1.111	1.008	5.1	2.90			
C-43	0.999	1.001	4.2	2.67	3.58	0.75	-92.22%
	0.998	1.003	5.6	3.56			
	0.996	1.008	7.1	4.50			
C-44	1.013	1.037	39.0	23.61	26.12	2.59	-43.23%
	1.013	1.052	42.0	25.07			
	1.014	1.035	49.0	29.69			
C-45	1.112	1.008	62.0	35.18	41.46	4.46	- 9.92%
	1.113	1.007	79.5	45.11			
	1.009	1.001	70.0	44.08			
C-46	1.048	1.038	85.0	49.70	50.29	3.21	+ 9.28%
	1.057	1.027	93.0	54.49			
	1.023	1.052	79.0	46.69			

1	2	3	4	5	6	7	8
C-47	1.011	1.016	72.0	45.29	46.02	3.99	+ 0.00%
	1.009	1.017	67.0	41.53			
	1.003	1.015	82.0	51.23			

TABLE # 5.1.3

COMPRESSIVE STRENGTH OF 5 cms. x 5 cms. x 5 cms.
CEMENT - SAND MORTAR CUBE.

1. Cement: Sand = 1 : 3

2. Cement: Water = 1 : 0.5652

3. Cross-head speed. = 0.5 mm/minute.

S.No.	Cement No.	3-days ± 1hr. compressive strength in $Kgf./cm^2$	Average 3-days compressive strength in $Kgf./cm^2$	7-days ± 2hrs. compressive strength (C.S) in $Kgf./cm^2$	Average 7-days compressive str. in $Kgf./cm^2$
1.	C-47	28.0	28.2	40.0	40.5
2.	C-47	28.4		41.0	
3.	C-46	40.0	39.5	58.0	59.0
4.	C-46	39.0		60.0	

TABLE # 5.1.4

COMPRESSIVE STRENGTH OF 5 cms. x 5 cms. x 5 cms.
CEMENT - SAND MORTAR CUBE.

1. Cement : Sand   =   1 : 3
2. Cement : Water   =   1 : 0.5
3. Cross-head speed   =   0.5 mm/minute.

S.No.	Cement No.	3-days ± 1hr. compressive strength in Kgf./cm^2	Average 3-days compressive strength in Kgf./cm^2	7-days ± 2 hrs. compressive strength (C.S) in Kgf./cm^2	Average 7-days compressive str. in Kgf/cm^2
1.	C-47	35.0	34.5	48.5	48.75
2.	C-47	34.0		49.0	
3.	C-46	58.0	58.5	64.0	64.0
4.	C-46	59.0		64.0	

TABLE # 5.1.5

X-ray analysis data for the study of depletion of raw material phases in cement clinkers.

1. Chromium Target, $(K\alpha_1) = 2.291002$ Å
2. Time Constant   =   3 seconds.
3. Scanning Speed   =   0.6°/minute.
4. Counts/second   =   100.

(Peak heights are given in mm.)

Note: BM means that the peak height is indistinguishable due to the back-ground effect.

Phases	d-values Å	Raw materials	C-1	C-2	C-3
CaO	2.778	146 - 160	6.5	5.5	4.0
	2.405	338 - 371	18.1	14.5	10.5
$CaCO_3$	3.035	1500 - 1646	33.0	30.0	13.5
	2.095	113 - 124	10.5	10.5	4.5
SiO_2	1.815	49.4	2.5	4.0	4.5
	1.378	39.5	2.1	2.2	2.1
χ-Al_2O_3	3.479	25.5	3.0	6.0	4.5
	1.601	28.7	4.0	3.0	6.0
β-Al_2O_3	2.820	9.0	2.0	2.0	4.5
	2.420	19.8	4.5	6.0	2.0
γ-Al_2O_3	2.450	19.0	7.0	3.5	6.5
	1.388	7.5	2.0	2.0	2.0
$KC_{23}S_{12}$	1.959	2.0	1.0	1.5	1.0
NC_8A_3	1.558	2.0	1.0	1.0	1.5

Phases	d-values Å	C-4	C-7	C-10	C-13	C-16
CaO	2.778	7.5	6.1	6.5	3.5	BM
	2.405	21.0	16.5	18.0	10.0	3.0
$CaCO_3$	3.035	23.0	32.0	11.0	10.0	5.0
	2.095	6.0	10.5	9.0	3.0	BM
SiO_2	1.815	4.0	2.5	5.0	2.0	2.0
	1.378	BM	2.0	2.0	2.0	3.0
$\chi-Al_2O_3$	3.479	3.0	4.0	1.5	1.5	1.5
	1.601	7.0	3.5	3.5	2.5	5.0
$\beta-Al_2O_3$	2.820	2.5	2.0	4.5	5.0	5.0
	2.420	2.0	5.0	4.0	3.5	3.0
$\gamma-Al_2O_3$	2.450	7.0	5.5	7.5	9.0	5.5
	1.388	2.5	2.0	2.0	1.5	2.0
$KC_{23}S_{12}$	1.959	1.0	2.0	BM	1.0	BM
NC_8A_3	1.558	1.0	1.0	BM	1.0	BM

Phases	d-values Å	C-17	C-21	C-24	C-27	C-28
CaO	2.778	BM	4.5	8.0	68.0	50.5
	2.405	8.0	12.0	24.0	201.5	168.0
$CaCO_3$	3.035	BM	14.0	5.0	15.5	9.5
	2.095	4.0	9.0	6.0	5.5	5.0
SiO_2	1.815	2.0	3.0	4.0	1.0	2.0
	1.378	3.0	2.0	2.0	2.0	1.0
$\times$-Al_2O_3	3.479	1.2	1.0	1.0	1.5	1.0
	1.601	5.0	3.2	4.0	3.5	3.8
β-Al_2O_3	2.820	5.5	4.0	3.5	4.5	5.0
	2.420	3.5	3.0	4.0	3.0	2.0
γ-Al_2O_3	2.450	6.2	7.8	7.0	7.0	8.5
	1.388	2.5	1.0	3.0	3.0	3.2
$KC_{23}S_{12}$	1.959	1.0	1.0	2.0	1.0	2.0
NC_8A_3	1.558	1.0	2.5	2.0	1.5	1.0

Phases	d-values Å	C-29	C-30	C-32	C-35	C-38
CaO	2.778	45.5	13.0	8.0	10.0	21.5
	2.405	137.0	37.0	23.0	29.0	65.0
$CaCO_3$	3.035	4.0	11.0	BM	15.0	4.0
	2.095	5.0	7.0	2.5	4.0	2.5
SiO_2	1.815	1.0	3.5	2.5	1.0	1.5
	1.378	3.0	2.0	1.0	2.5	2.5
$\chi-Al_2O_3$	3.479	1.0	1.0	1.5	2.0	1.5
	1.601	4.0	4.5	4.5	3.5	4.0
$\beta-Al_2O_3$	2.820	5.5	4.0	5.5	4.5	3.5
	2.420	3.5	2.5	5.5	2.0	3.0
$\gamma-Al_2O_3$	2.450	7.0	7.5	5.5	4.0	5.5
	1.388	3.5	3.8	2.0	1.0	1.5
$KC_{23}S_{12}$	1.959	2.0	1.5	2.5	2.0	1.0
NC_8A_3	1.558	2.0	2.5	2.5	3.0	1.5

Phases	d-values Å	C-39	C-46	C-47
CaO	2.778	17.0	9.0	BM
	2.405	50.0	26.0	3.0
$CaCO_3$	3.035	5.0	BM	12.0
	2.095	2.0	2.0	3.0
SiO_2	1.815	2.5	1.5	2.0
	1.378	2.5	2.0	1.5
$X-Al_2O_3$	3.479	3.0	1.5	2.5
	1.601	2.0	3.0	1.5
$\beta-Al_2O_3$	2.820	4.5	3.0	4.0
	2.420	2.5	2.5	3.0
$\gamma-Al_2O_3$	2.450	6.0	5.0	2.5
	1.388	1.5	2.5	2.0
$KC_{23}S_{12}$	1.959	2.0	2.5	3.0
NC_8A_3	1.558	2.0	1.5	2.0

TABLE # 5.1.6

X-Ray Analysis data for the study of the Cementing Phases
in Cement Clinkers

1. Chromium Target, $(K\alpha_1) = 2.291002$ Å

2. Time Constant = 3 seconds.

3. Scanning Speed = 0.6°/minute.

4. Counts /seconds = 100.

(Peak heights are given in mm.)

Note: BM means that the peak height is indistinguishable
due to the back-ground effect.

Phases	d-values Å	C-1	C-2	C-3	C-4	C-5	C-6
C_3S	3.020	12.0	14.0	7.0	18.0	19.0	14.0
	2.178	3.0	4.0	1.5	5.0	5.0	4.5
$\chi-C_2S$	2.700	30.0	34.5	20.0	59.0	61.0	43.0
	2.810	17.0	23.0	7.0	16.0	17.0	15.0
$\beta-C_2S$	2.780	46.0	54.0	39.0	45.0	47.0	43.0
	2.182	16.0	23.0	9.0	8.0	9.0	8.0
$\gamma-C_2S$	2.740	50.0	52.0	35.0	38.0	40.0	48.0
	3.000	22.0	27.0	6.0	11.0	13.0	12.0
C_3A	1.554	9.0	10.0	5.0	6.0	6.0	4.0
	1.204	5.0	5.5	3.0	4.0	4.0	2.0
C_5A_3	2.670	12.0	18.0	18.0	9.0	10.0	13.0
	2.980	4.0	6.5	6.0	1.0	4.5	3.0
C_2F	1.940	7.0	12.0	9.0	5.0	9.5	7.0
	1.840	3.0	3.0	1.0	1.0	2.0	2.0
C_4AF	2.630	7.0	12.0	11.0	BM	BM	BM
	1.572	3.0	3.0	4.0	5.0	7.0	1.0

Phases	d-values Å	C-8	C-10	C-13	C-14	C-15
C_3S	3.020	13.0	10.0	10.0	12.0	9.0
	2.178	3.0	3.0	4.0	4.0	3.5
$\alpha-C_2S$	2.700	65.0	35.0	70.0	71.0	68.0
	2.810	15.0	12.0	16.0	17.0	14.0
$\beta-C_2S$	2.780	50.0	42.0	46.0	50.0	40.0
	2.182	9.0	11.0	7.0	6.0	5.0
$\gamma-C_2S$	2.740	31.0	38.0	45.0	45.0	55.0
	3.000	6.0	11.0	13.0	10.0	14.0
C_3A	1.554	10.0	5.0	7.0	8.0	5.0
	1.204	4.0	BM	BM	3.0	2.0
C_5A_3	2.670	14.0	10.0	12.0	10.0	9.0
	2.930	2.0	2.0	5.0	4.0	3.0
C_2F	1.940	8.0	7.0	15.0	18.0	10.0
	1.840	3.0	3.0	2.0	2.0	2.0
C_4AF	2.630	8.0	3.0	4.5	6.0	3.5
	1.572	2.0	BM	1.5	1.5	BM

Phases	d-values Å	C-16	C-17	C-18	C-19	C-20
C_3S	3.020	28.0	24.0	17.0	16.0	20.0
	2.178	14.0	15.5	10.0	8.0	5.0
α-C_2S	2.700	7.0	9.0	9.0	9.0	29.0
	2.810	4.0	6.0	5.5	6.5	14.0
β-C_2S	2.780	241.0	234.0	256.0	115.0	50.0
	2.182	68.0	40.0	43.5	21.0	10.5
γ-C_2S	2.740	24.0	37.0	30.0	44.5	52.0
	3.000	9.0	9.0	8.0	15.5	14.0
C_3A	1.554	6.0	3.0	8.0	5.0	6.5
	1.204	2.5	BM	3.0	1.5	2.5
C_5A_3	2.670	28.0	17.0	18.0	14.0	16.0
	2.980	8.0	7.5	8.0	5.0	5.5
C_2F	1.940	16.0	16.0	18.5	14.0	9.0
	1.840	1.0	BM	2.0	BM	1.5
C_4AF	2.630	2.5	4.0	3.0	4.5	4.5
	1.572	BM	1.5	1.5	BM	2.0

Phases	d-values Å	C-22	C-25	C-29	C-30	C-32
C_3S	3.020	12.0	15.0	5.0	5.0	5.5
	2.178	4.0	3.5	8.0	4.5	5.0
$\lambda\text{-}C_2S$	2.700	43.0	23.5	29.0	7.5	9.5
	2.810	17.5	10.5	12.5	6.0	6.5
$\beta\text{-}C_2S$	2.780	45.0	118.0	35.0	201.5	67.5
	2.182	11.0	34.5	14.0	49.5	29.5
$\gamma\text{-}C_2S$	2.740	44.0	46.0	51.5	66.0	38.0
	3.000	9.0	11.5	14.5	18.5	8.0
C_3A	2.670	9.0	10.5	5.0	5.0	16.0
	1.204	3.0	2.5	BM	1.5	9.5
C_5A_3	2.670	13.5	5.0	5.0	15.5	28.0
	2.980	4.0	BM	1.5	10.0	19.5
C_2F	1.940	7.5	5.0	5.0	16.0	26.5
	1.840	2.5	1.5	BM	9.5	13.5
C_4AF	2.630	5.0	7.0	2.0	8.0	6.0
	1.572	1.0	2.0	BM	2.5	2.5

Phases	d-values Å	C-35	C-38	C-39	C-46	C-47
C_3S	3.020	4.5	3.0	3.0	6.0	19.5
	2.178	2.0	2.0	2.0	5.0	8.0
α-C_2S	2.700	12.0	11.0	8.5	8.0	4.0
	2.810	7.0	5.0	7.0	7.0	5.5
β-C_2S	2.780	64.0	14.0	19.0	55.0	22.5
	2.182	18.	14.0	14.0	15.0	12.5
γ-C_2S	2.740	35.0	35.5	34.0	21.0	41.0
	3.000	4.0	4.0	5.0	6.0	5.5
C_3A	1.554	6.5	6.0	4.5	3.0	4.0
	1.204	3.0	3.5	2.0	1.5	2.5
C_5A_3	2.670	15.0	2.0	2.5	12.0	6.0
	2.980	5.0	2.0	2.0	8.5	4.0
C_2F	1.940	10.5	4.5	5.5	9.0	3.5
	1.840	5.0	2.0	4.0	2.0	2.5
C_4AF	2.630	5.0	4.0	6.5	10.0	BM
	1.572	2.0	2.5	5.0	3.0	2.5

TABLE # 5.1.7

COLOUR ANALYSIS OF CEMENTS

Cement No.	Colour Swatch reference.	Colour name
C-1	30 A 2	Greenish white
C-2	30 A 2	Greenish white
C-3	30 C 3	Water green
C-4	30 A 1	White
C-5	30 A 1	White
C-6	30 A 1	White
C-7	30 C 3	Water green
C-8	30 C 3	Water green
C-9	30 B 4	Grayish green
C-10	30 A 3	Pale green
C-11	30 A 3	Pale green
C-12	30 A 4	Pastel green
C-13	30 B 1	Grayish white
C-14	30 B 1	Grayish white
C-15	30 B 1	Grayish white
C-16	9 B 2	Reddish gray
C-17	9 B 2	Reddish gray
C-18	9 B 2	Reddish gray
C-19	9 B 2	Reddish gray
C-20	1 A 1	White
C-21	24 A 2	Turquoise white

Cement No.	Colour Swatch reference	Colour name
C-22	24 A 2	Turquoise white
C-23	25 A 2	Greenish white
C-24	26 A 2	Greenish white
C-25	26 A 2	Greenish white
C-26	27 A 2	Greenish white
C-27	27 B 1	Grayish white
C-28	27 B 1	Grayish white
C-29	27 B 1	Grayish white
C-30	9 B 2	Reddish gray
C-31	9 B 2	Reddish gray
C-32	10 A 2	Pinkish white
C-33	10 B 2	Reddish gray
C-34	10 B 2	Reddish gray
C-35	10 B 2	Reddish gray
C-36	15 A 2	Violet white
C-37	15 B 2	Lilac gray
C-38	15 A 1	White
C-39	15 A 1	White
C-40	15 A 1	White
C-41	15 A 1	White
C-42	15 A 1	White
C-43	15 A 1	White
C-44	15 B 2	Lilac gray
C-45	15 A 2	Violet white
C-46	13 B 2	Purplish gray

TABLE # 5.1.9

ANALYSIS OF FRIABILITY AND WORKABILITY

Cement No.	Friability	Workability
C-1	Friable and porous	Requires less water for plasticity.
C-2	-do-	-do-
C-3	-do-	-do-
C-4	Friable	Normal
C-5	-do-	-do-
C-6	Very hard	-do-
C-7	Friable and porous	Requires less water for plasticity.
C-8	Not very friable	-do-
C-9	-do-	-do-
C-10	Friable and porous	-do-
C-11	-do-	-do-
C-12	-do-	-do-
C-13	Friable	Requires a little excess water for plasticity.
C-14	-do-	-do-
C-15	-do-	-do-
C-16	Friable, but not very soft.	Normal
C-17	Friable	-do-
C-18	-do-	-do-
C-19	Friable but not very soft.	-do-

Cement No.	Friability	Workability
C-20	Friable	Normal
C-21	-do-	Very plastic
C-22	-do-	-do-
C-23	Friable but not very soft.	-do-
C-24	Not porous, quite hard	Quick setting
C-25	-do-	-do-
C-26	Very hard	-do-
C-27	Friable	Very plastic but not sticky
C-28	-do-	-do-
C-29	-do-	Takes excess water to begin with
C-30	Porous and friable	Requires lots of water for plasticity
C-31	-do-	-do-
C-32	Friable	Normal
C-33	-do-	-do-
C-34	Quite hard	-do-
C-35	Porous and friable	Very sticky and requires lots of water for plasticity
C-36	-do-	-do-
C-37	-do-	-do-
C-38	Friable	Very plastic but initially requires more water

Cement No.	Friability	Workability
C-39	Friable	Very plastic, slippery, but gives false setting within a minute
C-40	-do-	-do-
C-41	-do-	Very plastic and slippery
C-42	-do-	-do-
C-43	-do-	-do-
C-44	Hard	Requires lots of water for plasticity
C-45	Very hard	Initially requires more water for plasticity
C-46	Friable	Normal
C-47	-	Requires more water for plasticity

5.2 DISCUSSION:

5.2.1 Effect of Flux:

As can be seen clearly from figures 5.4 and
5.5, given in page nos. 143 and 144, the flux plays a
very crucial role in the formation of the cementing
phases, through easy clinkerization. All the 5 fluxes
tried, proved to be beneficial at all stages of cement
setting and hardening. There was a marked difference in
their efficiency however, when added at 2 wt.% level,
replacing CaO.

Sodium Silico-fluoride is by far the best flux.
It is at its best when the clinkers are rapidly cooled.
Calcium phosphate follows closely, through it does not
display any extra ordinary effect for rapidly cooled
clinkers. Boric acid is much better than magnesium
oxide and calcium fluoride. Magnesium oxide is slightly
superior to calcium fluoride at 3-days hardening, but
its superiority over calcium fluoride is enhanced after
7-days of curing. Though calcium fluoride was found to
be the least beneficial flux, yet its presence alone has
a significant effect, especially for the clinkers which
are cooled at moderate rates.

The important thing to be noticed is that all
these fluxes do not prove to be sufficiently effective
at 1350°C with one hour firing, when compared with A C C
white portland cement. This temperature is low when
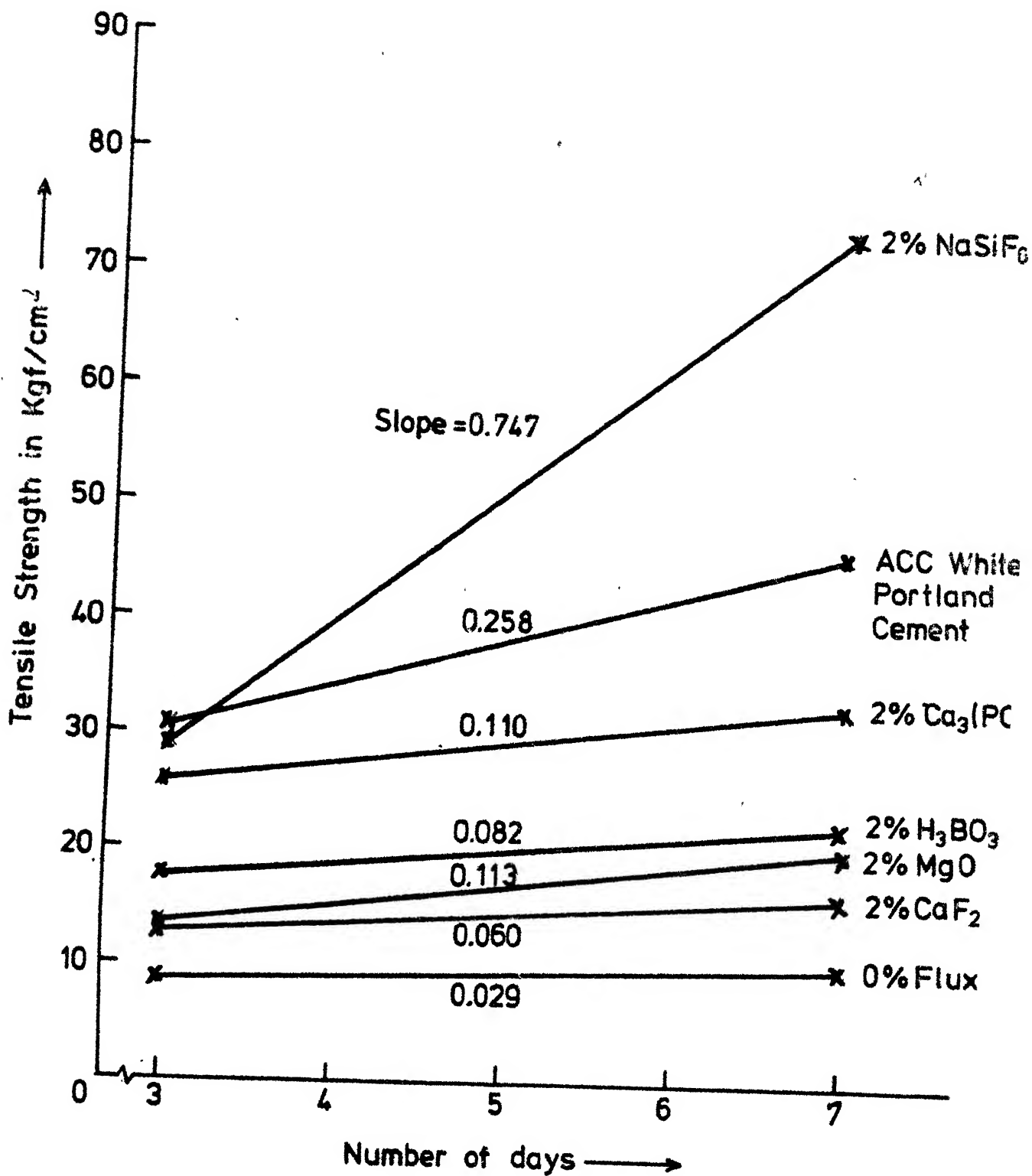
Fig. 5.1 Effect of flux on development of Strength in air cooled cements.
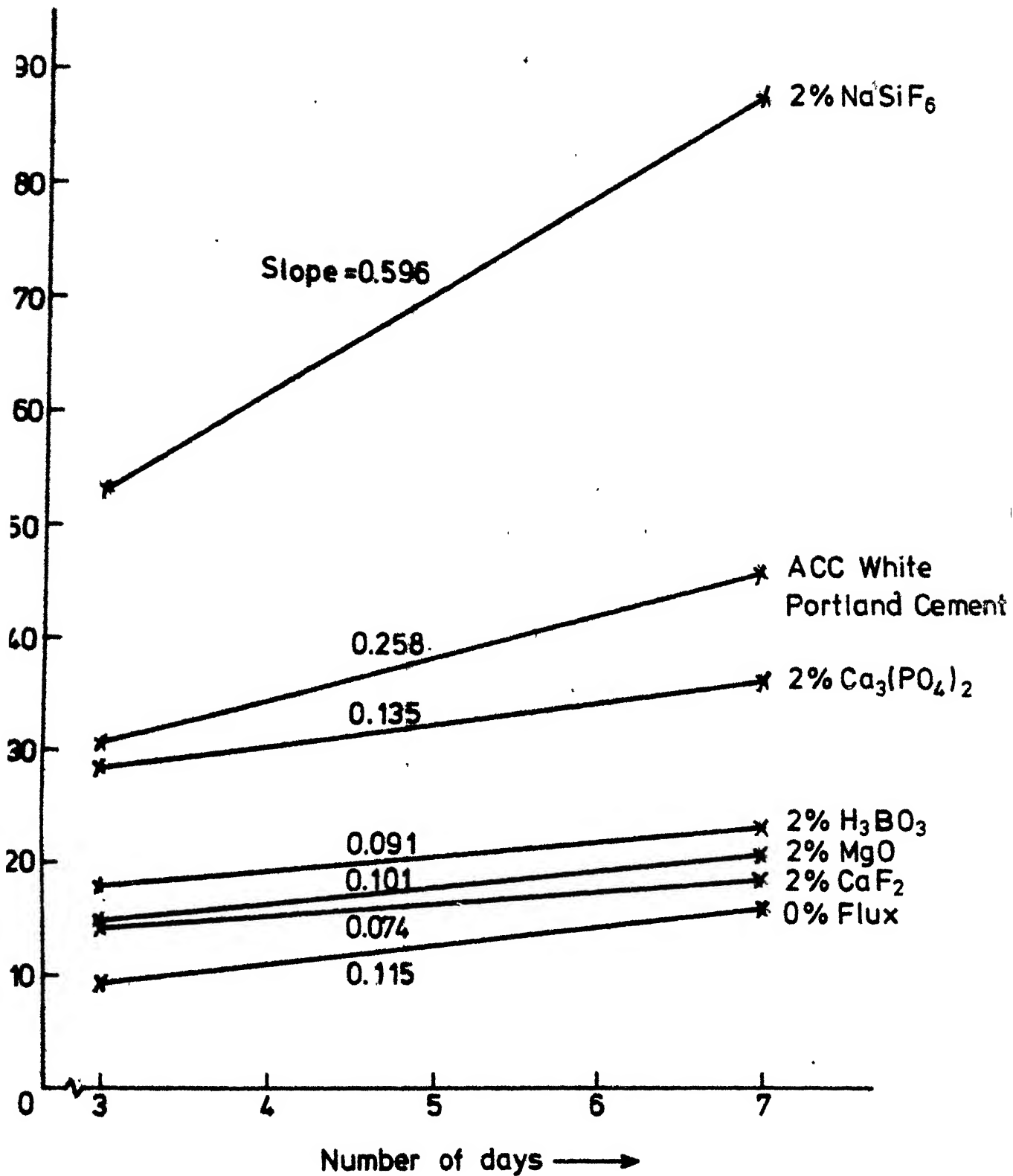
Fig. 5.2 Effect of flux on development of strength in fan cooled cements.
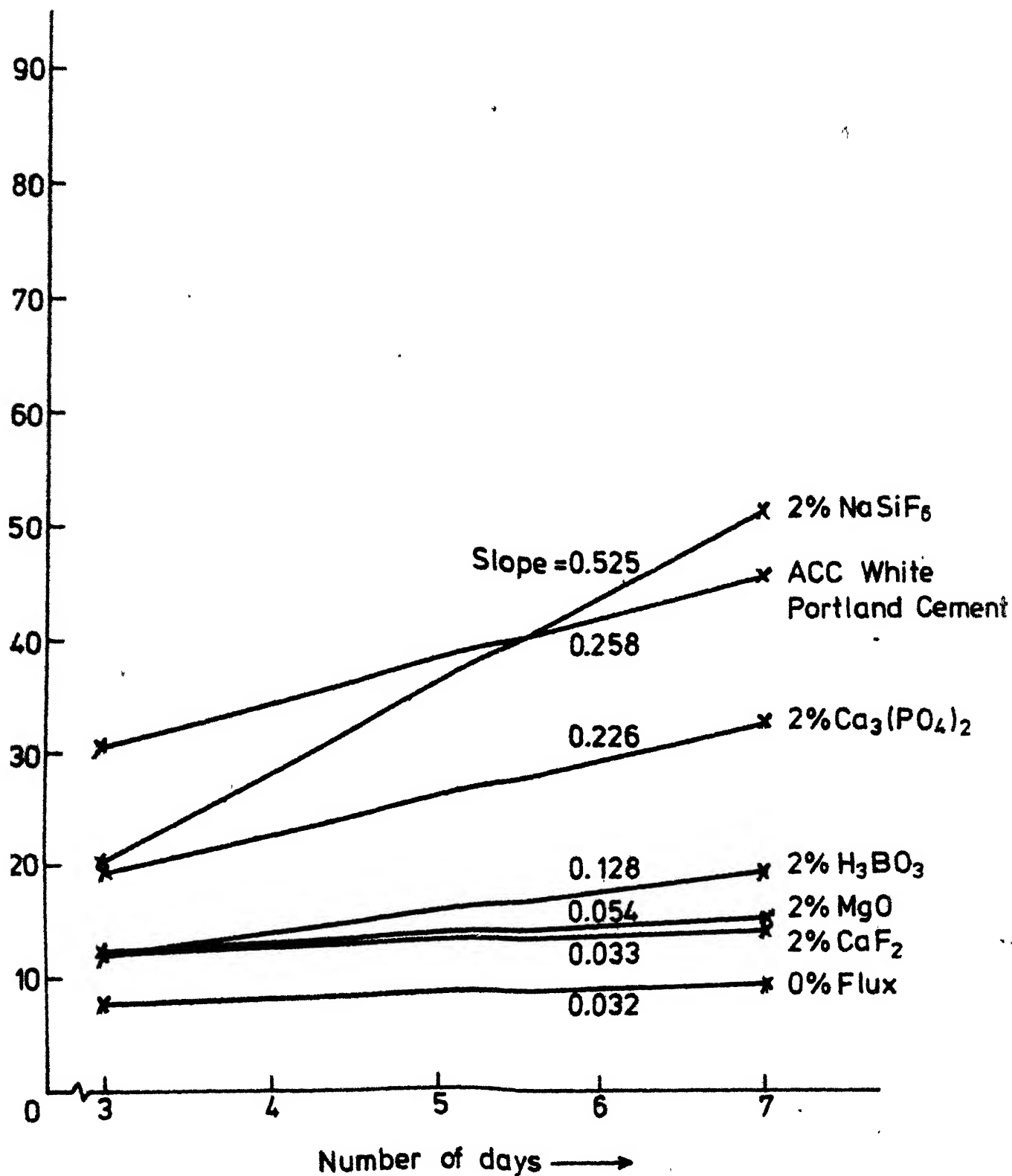
Fig. 5.3 Effect of flux on development of strength in furnace cooled cements.
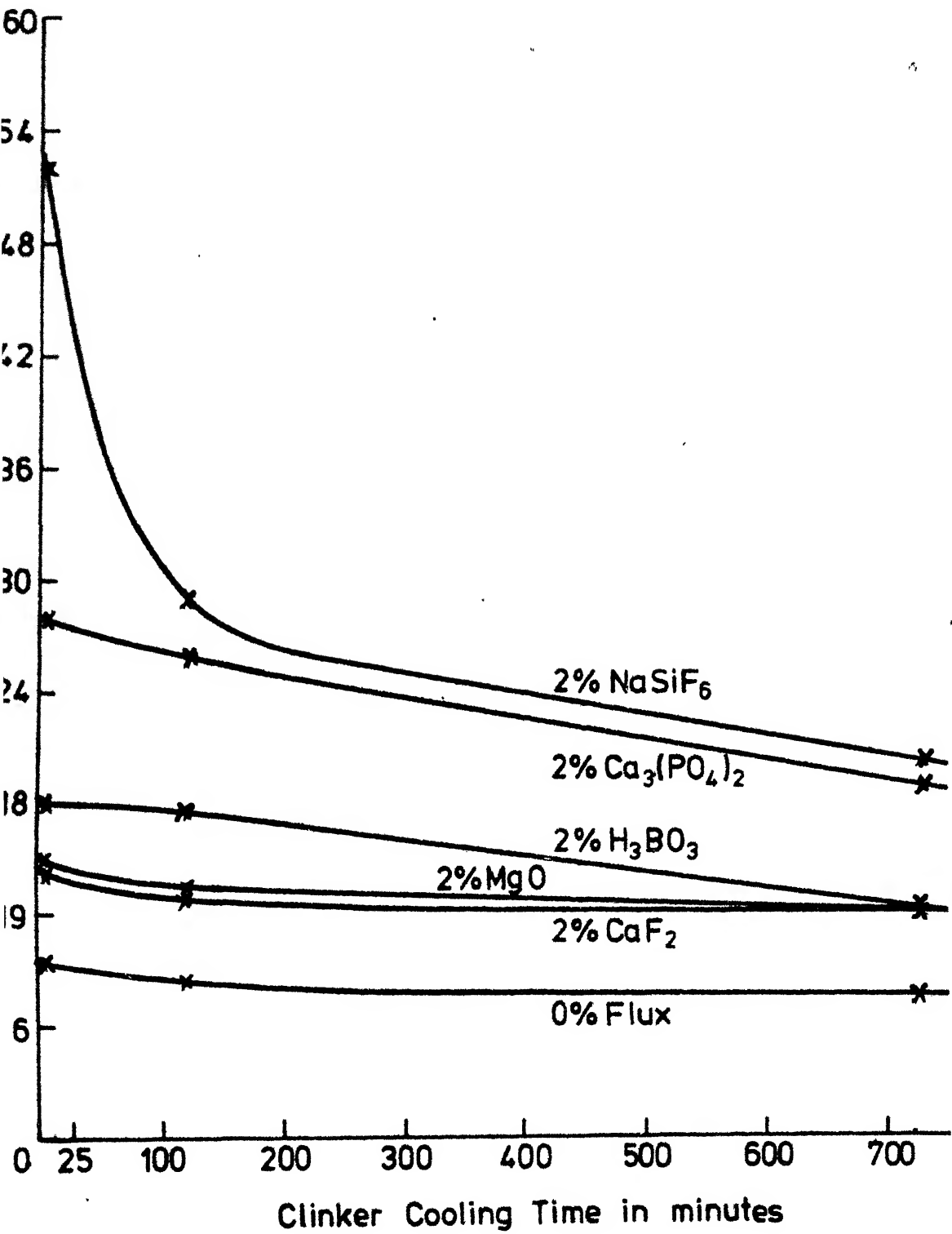
Fig. 5.4 Effects of flux and heat treatment on the
         3-days stength.
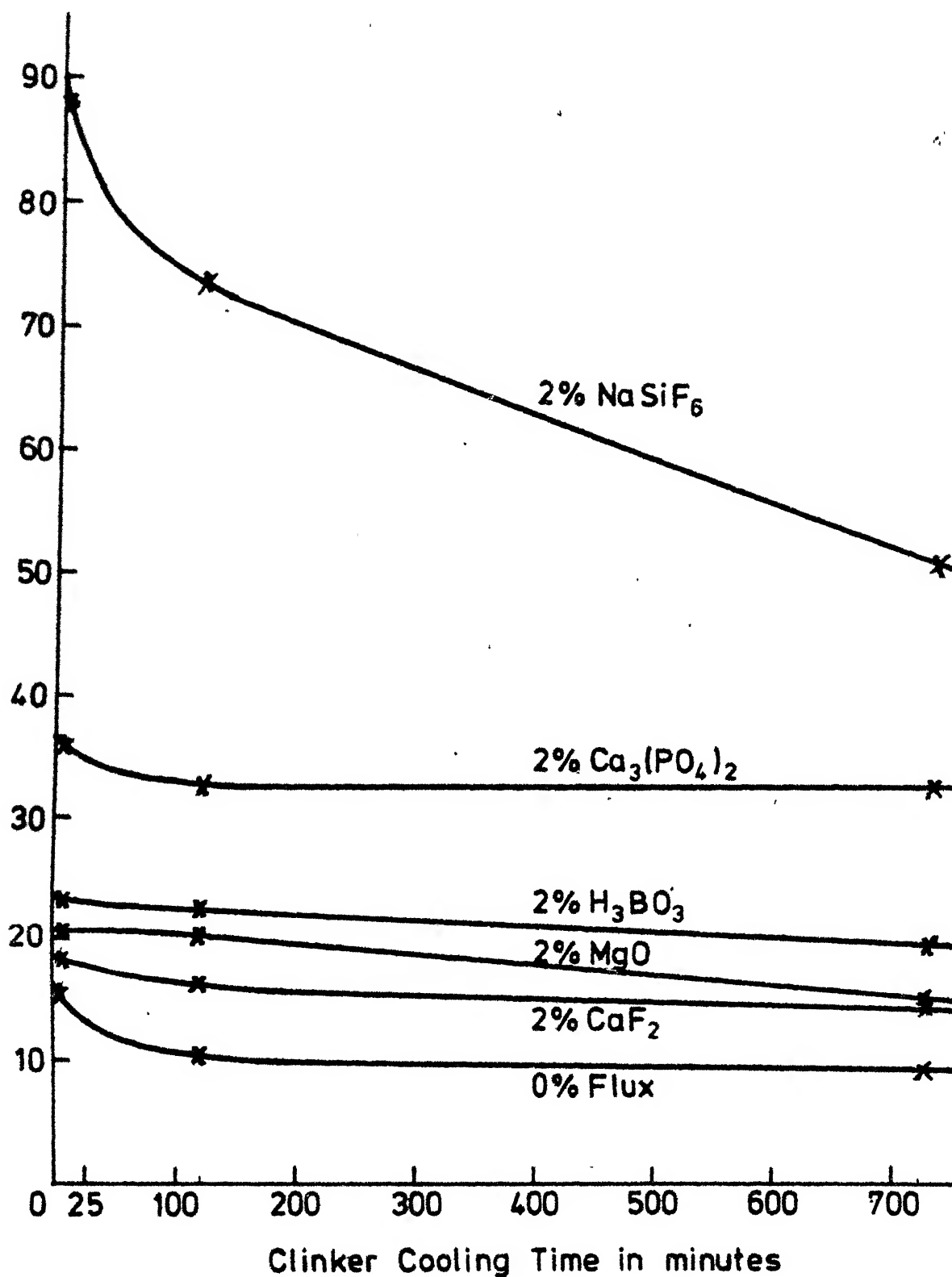
Fig. 5.5 Effects of flux and heat treatment on the 7-days strength.

compared with 1500°C used for white portland cement production. As can be seen from figures 5.1, 5.2 and 5.3 given in pages 140, 141 and 142, only fan cooled sample, containing 2 wt.% sodium silico-fluoride, is superior to A C C white portland cement, at all ages. The air cooled and the furnace cooled samples, containing 2 wt.% $NaSiF_6$, cross the ACC white portland cement, in terms of strength after 3.25 days and 5.75 days of curing respectively.

Most fluxes as expected, tend to be more effective when clinkers are rapidly quenched in air. As already mentioned, sodium silico-fluoride gives a tremendously high value of strength (about 57&.0% higher as compared to that with0% flux), for rapidly cooled clinkers, at 3-days and 7-days curing level. Even calcium phosphate, calcium fluoride, magnesium oxide display this feature. This is because, the fluxes, at low temperature of 1350°C, tend to facilitate the formation of $\beta - C_2 S$. With rapid cooling most of this β-phase is retained in tact, which in turn provides the higher strength. Because $NaSiF_6$ promotes maximum $\beta - C_2 S$ formation, as can be seen from Table No. 5.1.6, its heightened effect for rapidly cooled clinkers is obvious. This feature is present, due to the above reasoning, even when no flux is present.

By referring to figures 5.1, 5.2 and 5.3 one can easily see that the rate of development of strength is highest for the cement containing 2 wt.% sodium silico-fluoride. This out-standing rate of development of strength, as expected, is due to excessive formation of β-C_2S, which gains strength slowly. As can be seen from Table No. 5.1.6, page No. 131, calcium phosphate is next in the list of excessive β-C_2S formation, and therefore it also gives rise to a high rate of development of strength as can be seen from the plot pertaining to the furnace cooled cement. Though the rest of the fluxes, have slightly higher proportion of β-C_2S than that contained in the ACC white portland cement, yet the rate of development of strength due to them is not as high as that of ACC white portland cement. This is because, when presence of β-C_2S is not significantly larger in amount, the rate of development of strength is modified by the presence of other phases too.

The rate of development of strength, for a given amount of a specific flux is dependent on the cooling rate too. For instance, for cements containing 2 wt.% $NaSiF_6$, the rate of development of strength is very high for air cooled sample, so much so that it fast catches upon the higher strength of the rapidly quenched sample, after a period of time. This is because, as per

Table No. 5.1.6, air cooled sample has lower content
of $-C_2S$ but higher content of C_3S.

While sodium silico-fluoride turned out to be
the best flux, but it is not without its inconvience.
It tends to impart a pink tint to the cement. But then
as the process of setting under water progresses, this
tint vanishes within 1 day. Unless a modification is
brought about in the IS Specification: 8042-1978, it
cannot be called a white portland cement in the strict
sense. As can be seen from Table No. 5.1.7 even, MgO
tends to give a light green tint.

The presence of flux also affects the tap
density and the workability of the cements. The presence
of 2 wt.% $NaSiF_6$ reduces the tap density by 22.93%, The
effect of other fluxes can be seen from Table No. 5.1.8.
As far as the workability is concerned it is highly
improved when CaF_2 is used as a flux. The effect of
other fluxes can be seen from Table No. 5.1.9.

5.2.2 Effect of Heat Treatment:

As seen from figures 5.4 and 5.5, rapid quenching
of clinkers, is always beneficial, specially when using
$NaSiF_6$ as a flux. Rapid cooling prevents the $\beta-C_2S$ to
$\gamma-C_2S$ inversion. The three days strength is seem to be
more sensitive to heat treatment, because most of the
strength is due to $\beta-C_2S$.

Heat treatment of clinkers also determines the rate of development of strength. As can be seen from figures 5.1, 5.2 and 5.3, **given** a particular heat treatment, excepting for the furnace cooled samples and for cement containing $NaSiF_6$, all cements have more or less same rate of development of strength. This rate of development of strength is found to be higher for the fan cooled samples. This is again related to the inversion phenomena.

Furnace cooling tends to produce a hard, non-friable clinker with darker shades. This can be seen from Table Nos. 5.1.7 and 5.1.9.

5.2.3 Effect of Soaking Time:

Greater is the duration for which the clinker is held at the firing temperature, then further will be the extent of combination of the reacting species.

As can be seen from figures 5.6 and 5.7 given in page numbers 149 and 150, the effect of soaking time is enhanced positively, when a flux is used. Without a flux at 1200°C, with a soaking time extending beyond 3 hours, the strength begins to fall slowly. This results due to over-burning. The grains of free CaO formed out of dissociation of calcium silicates and aluminates, grow so much in size and become so large in quantity, that later as a result of it, during the time of cooling they cannot recombine to give back the cementing phases.
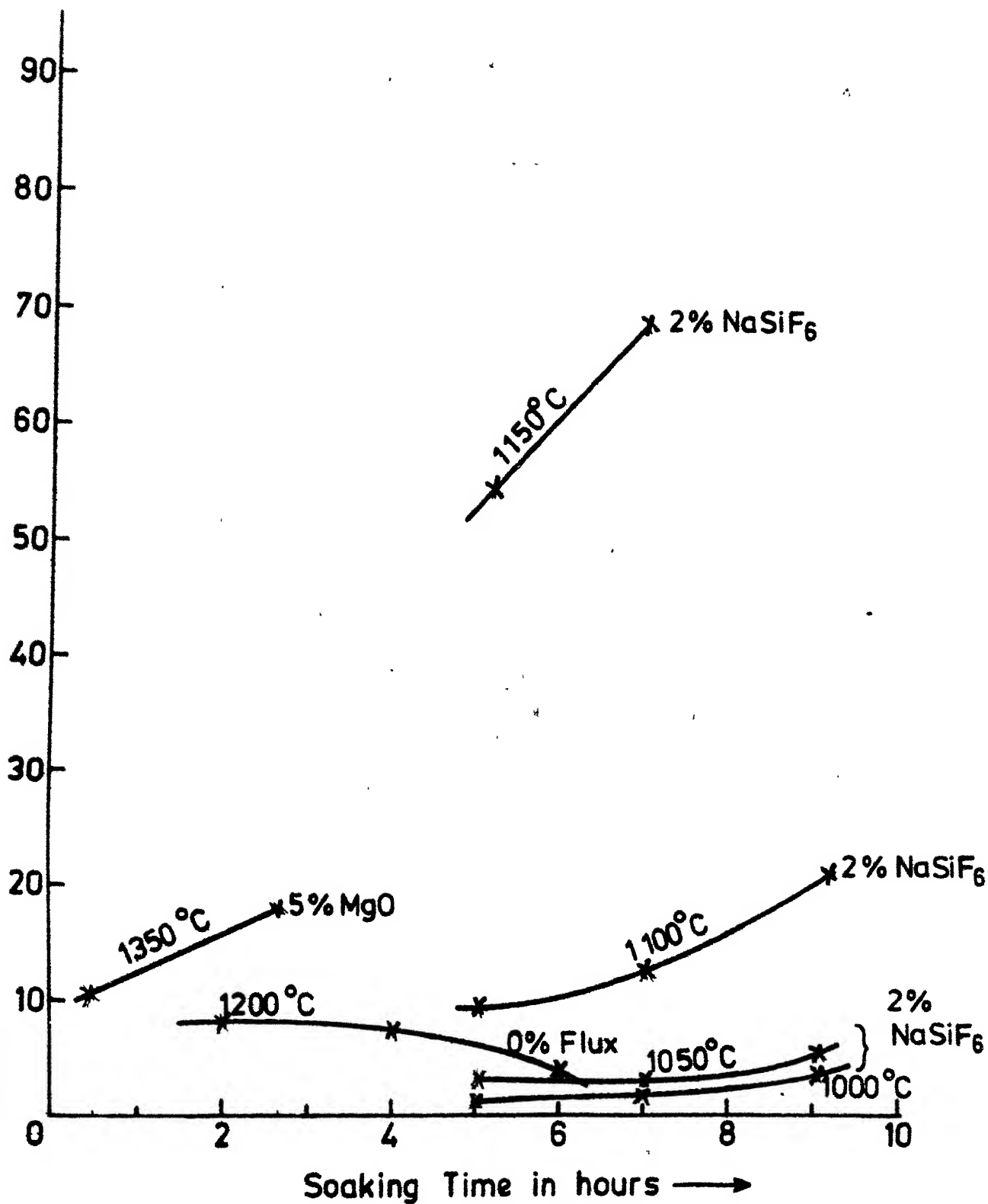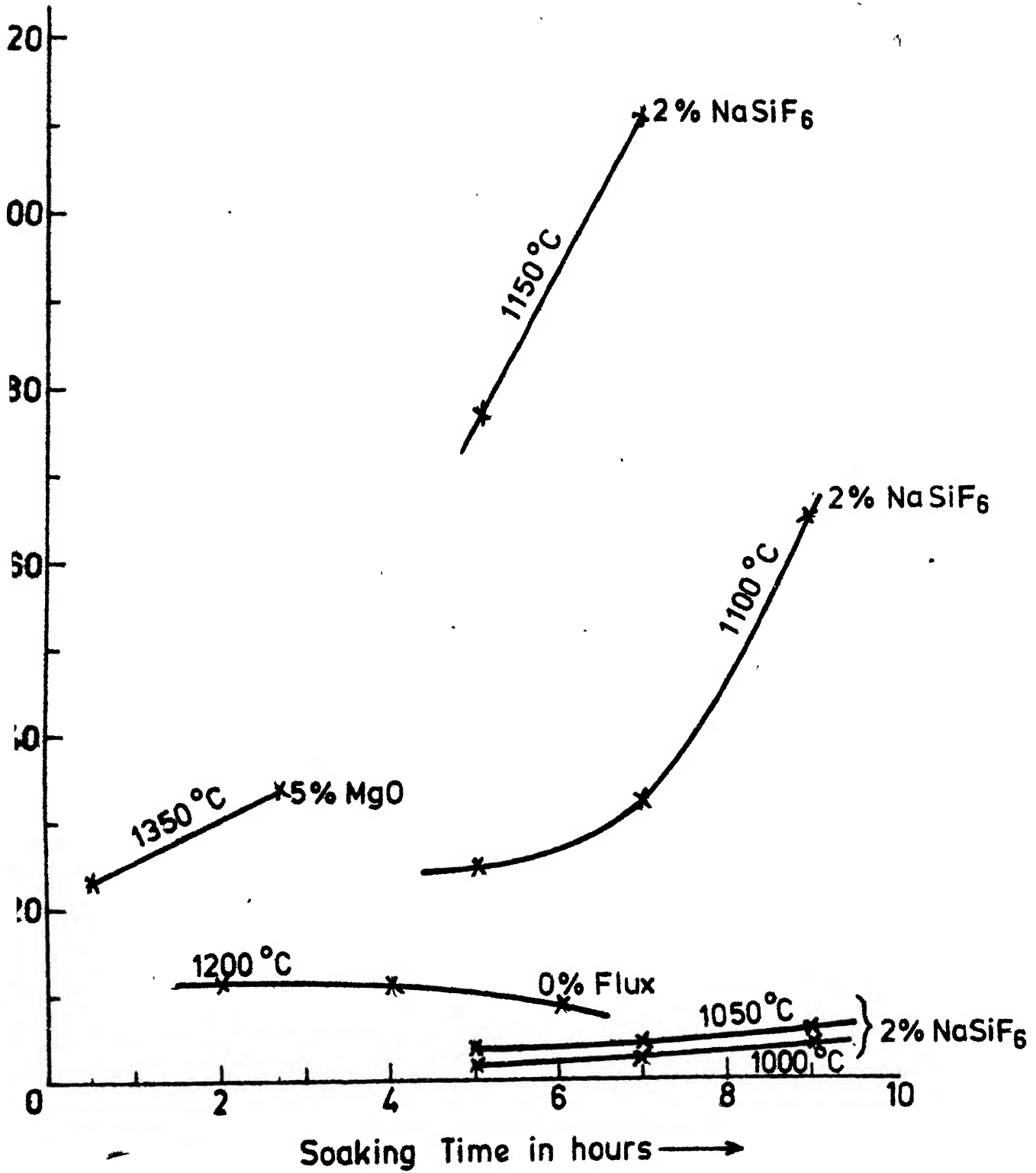
g. 5.7 Effect of soaking time on 7-days strength of air cooled

The extent to which the fluxes are effective is dependent on the firing temperature. That is, when held at the temperature at which the fluxing action, like the exchange mechanism of ions, is in operation, the effect of soaking time is at its maximum. It seems that with 2 wt.% $NaSiF_6$, the fluxing action takes place at 1100°C.
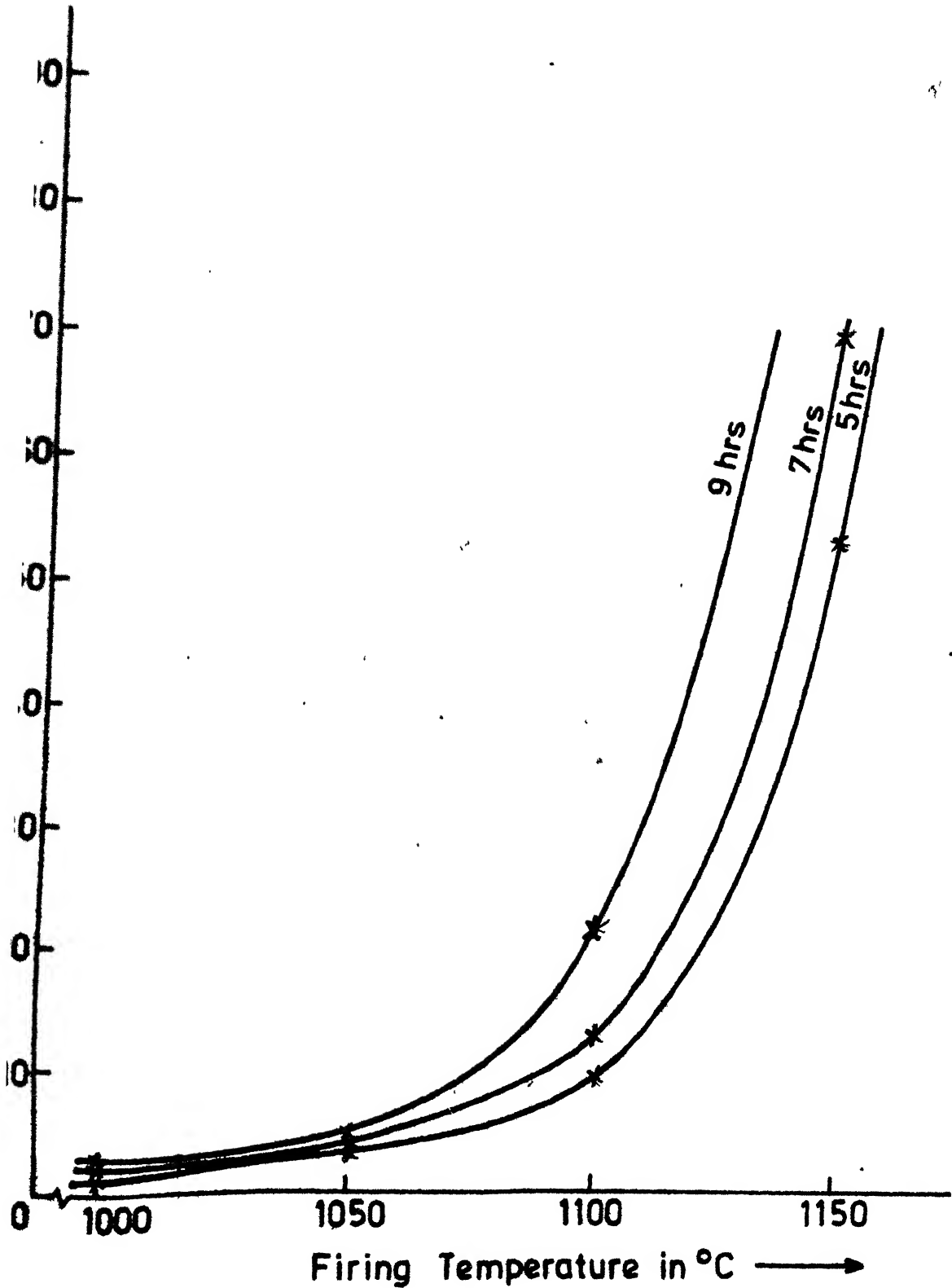
5.2.4 Effect of Temperature:

With rising temperature, the burnability of the cement clinker is vastly improved. This can be seen from Table No. 5.1.5. For instance, with 5 hours soaking time, as the temperature falls from 1150°C to 1100°C and finally to 1050°C, the CaO peak pertaining to d-value of 2.405 $\overset{\circ}{A}$ increases from 23 mm, to 29 mm and finally to 65 mm. The amount of free lime increases parabolically.

The same state of affairs is reflected in figures 5.8 and 5.9 given in page numbers 152 and 153. With increasing firing temperature, the strength of cement, and hence the amount of cementing phases increase parabolically.

Higher the soaking time more pronounced is the effect of the high temperature.

Higher the temperature, greater is the mobility of the reacting species. So the reaction kinetics is vastly improved with the rising temperature.

5.8 Effect of firing temperature on 3-days strength of air cooled cements containing 2% $NaSiF_6$ for different soaking time.

9 hrs

7 hrs

5 hrs

Firing Temperature in °C
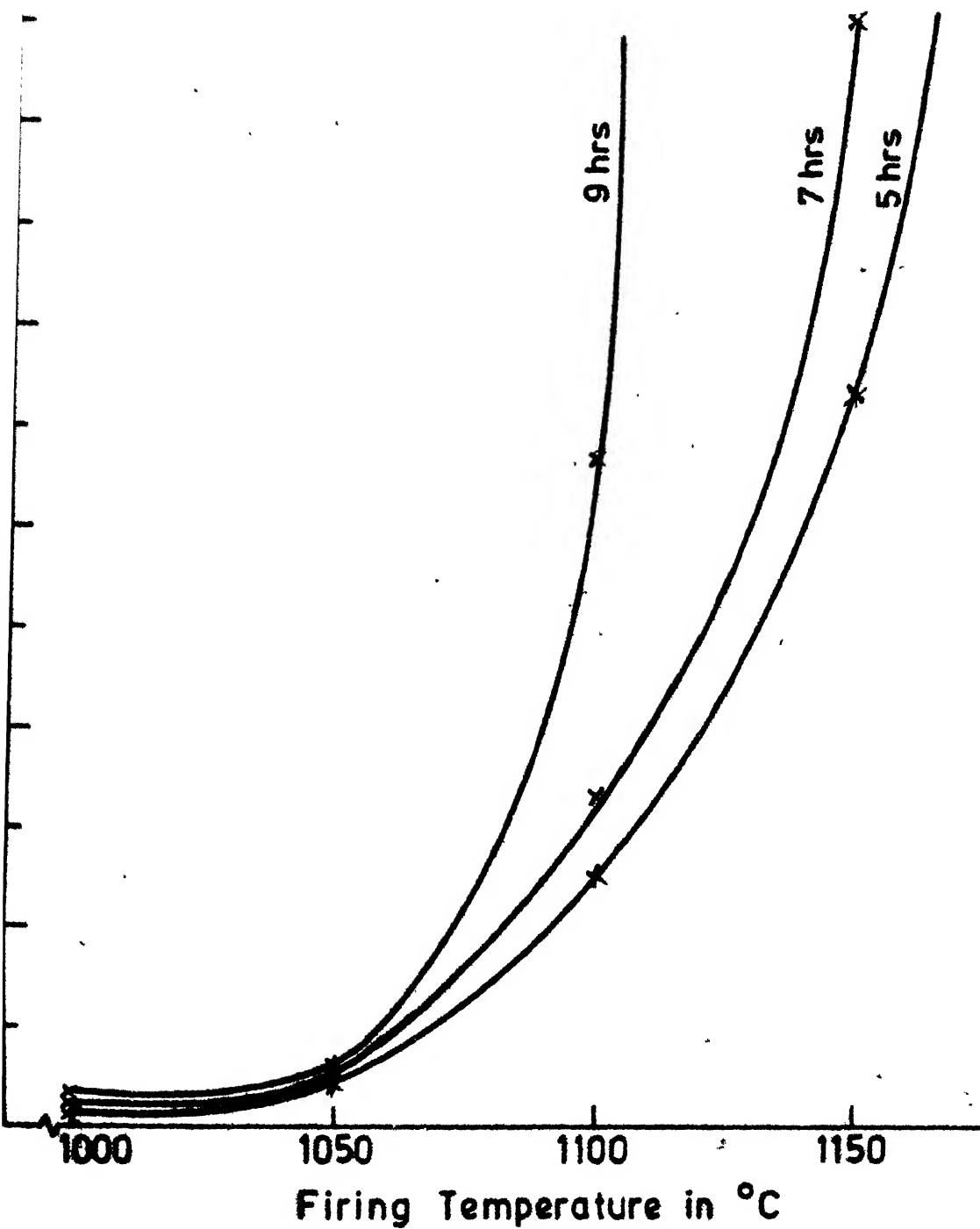
5.9 Effect of firing Temperature on 7-days strength of
air cooled cements containing 2% NaSiF₆ for
different soaking time.
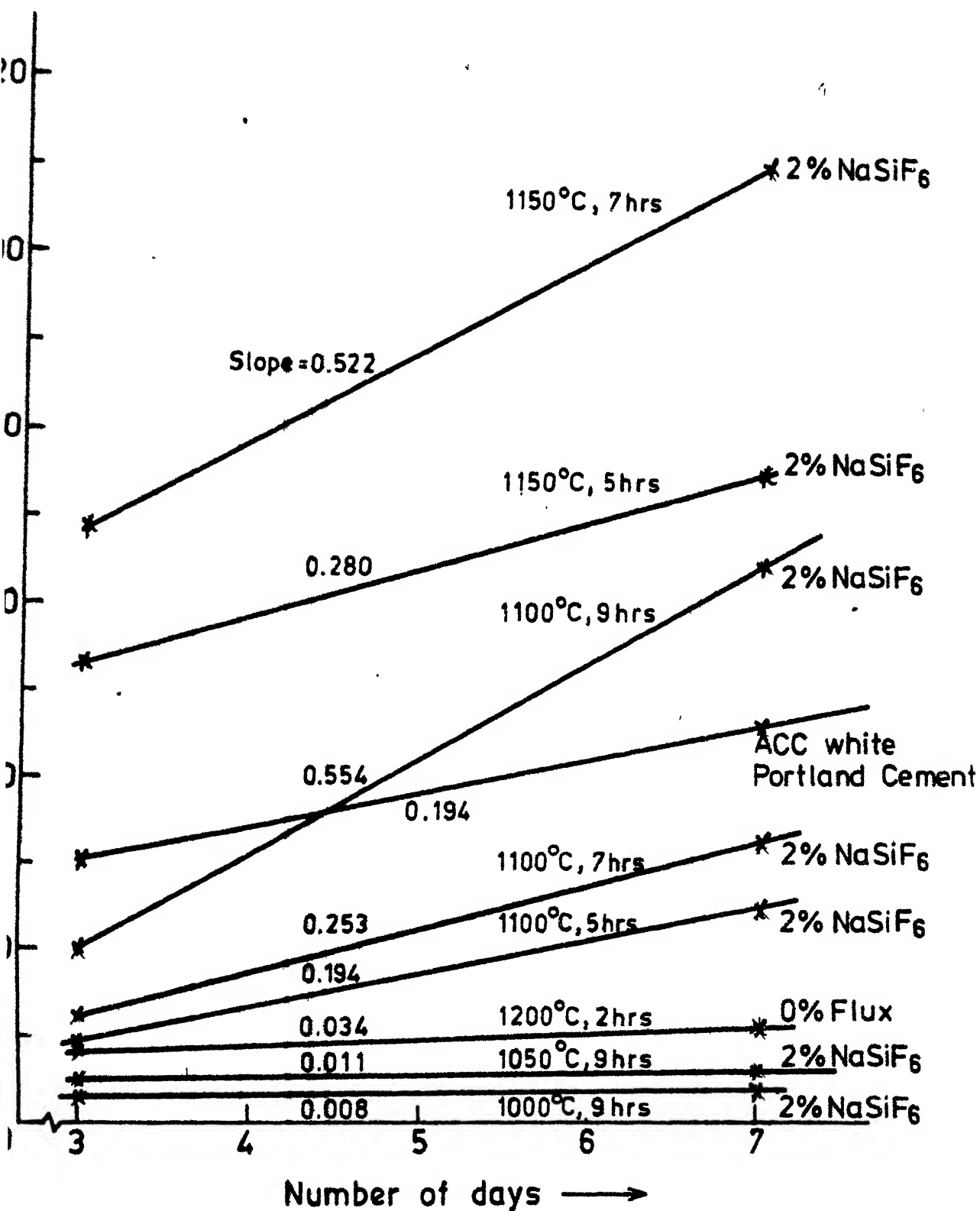
5.10 Effects of soaking time and firing temperature on the development of strength in air cooled cements.

As already mentioned, the efficacy of a flux is maximum only when there is a correct combination of both the firing temperature and the time. This can easily be seen from Figure No. 5.10 given in page No. 154. At temperatures as low as 1000°C to 1050°C, there is hardly any role of the temperature. The fact that at there is no development of strength with time, even after a soaking time of as much as 9 hours, shows that all the strength attained is only due to the formation of calcium aluminates. But at 1100°C, with 9 hours soaking time, the rate of development of strength is so high that, not with standing the fact that its 3-days strength is 34.8 wt.% less than that of ACC white portland cement, but only after 4.5-days its strength equals that of ACC cement. Again at 1150°C it is better to soak the clinker for 7-hours instead of 5 hours, because then not only the initial strength is higher but also the rate of development is higher.

5.2.5 Effect of Morphology of the Raw Materials:

As can be seen from Figure No. 5.11 given in page No.156, it is better to use commercial grade hydrated lime than G.R. grade quicklime. The latter is not only more expensive, but also because it is pure laboratory reagent it does not contain any impurity which could possibly act as flux. Quicklime is not in as much an activated state, as the hydrated lime is, because its specific surface area is not that high. As a result the solid state kinetics is

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lower with quicklime.

Even the rate of development of strength is slightly higher with the hydrated lime as compared to that with quicklime.

When unactivated + 200 mesh ASTM size Bayer's alumina, is used in place of activated - 100 mesh ASTM size Bayer's alumina, not only the strength but even the rate of development of strength falls significantly. This is because in presence of the other raw materials, which are well below -100 mesh ASTM in size, unactivated alumina gives rise to inhomogenous blending. This adversely affects the rate kinetics during the clinkering operation. Not only the formation of C_3A, the first melting liquid, is hindered but also the solid state reactions leading to the formation of C_5A_3 is effected adversely.

Besides with unactivated Bayer's alumina, the clinker developes a deeper pink tint. This is shown in Table No. 5.1.7 where the colour changes from reddish gray to lilac gray.

When black rice husk ash containing 30.5% SiO_2 is used in place of white rice husk ash containing 94% SiO_2, the strength falls by around 26%. The rate of development of strength is also lowered slightly. Besides the clinker formed is not only very hard, but even the colour is much deeper. As can be seen from Table No.5.1.7

the colour changes from reddish gray to violet white.

The carbonaceous, and organic matter retained in black rice husk ash, gives extra heat energy to the reacting species, thereby raising the local temperature. But then the extra heat is available with the raw material is at around 800°C. Since as per figure no. 3.3, it takes about 3.3 hours for the temperature of the raw feed to rise from 800°C to 1350°C, this excess heat released does not contribute significantly towards raising the maximum firing temperature, and thereby cannot contribute significantly towards enhancement of the rate kinetics. On the contrary, presence of the voids left behind by the volatized materials, increase the diffusion path between the reacting species, thereby adversely affecting the rate kinetics. Most probably the harm done by the increased diffusion path is not compensated by the benifit accruing out of excess heat generated with the voltatization of carbon and organic matters.

CHAPTER # VI

CONCLUSION AND SUGGESTIONS

The aim of the present work is to find a cheaper route for the production of white portland cement. Rice husk ash, Bayer's alumina and hydrated lime were used as raw materials along with a flux. The aim was not to produce a cement with the highest set of qualities, because if the quality is far in excess of what is required by the market, then it will necessitate extra expenditure during the process of production. So the aim was to produce a white portland cement, with a quality which is a bit superior to that of the A.C.C. product.

After a systematic search for the best flux, it was decided to use 2 wt.% sodium silico-fluoride. It not only gave the maximum strength but also gave the maximum strength development rate. It means that with time, its efficacy as a flux goes on improving rapidly. After 3-days of curing its strength is 73.73% higher and after 7-days of curing its strength is 88.82% higher than the corresponding values for the A.C.C. white portland cement. Even the X-ray analysis data supported its claim. When 2 wt.% $NaSiF_6$ is used as a flux, the peak pertaining to the $- C_2S$ phase is 11.66 times higher than that obtained in A.C.C. white portland cement. Even the peaks pertaining to C_3S, C_3A, C_5A_3 and C_2F are significantly higher than that obtained in A.C.C.

Compression in mm
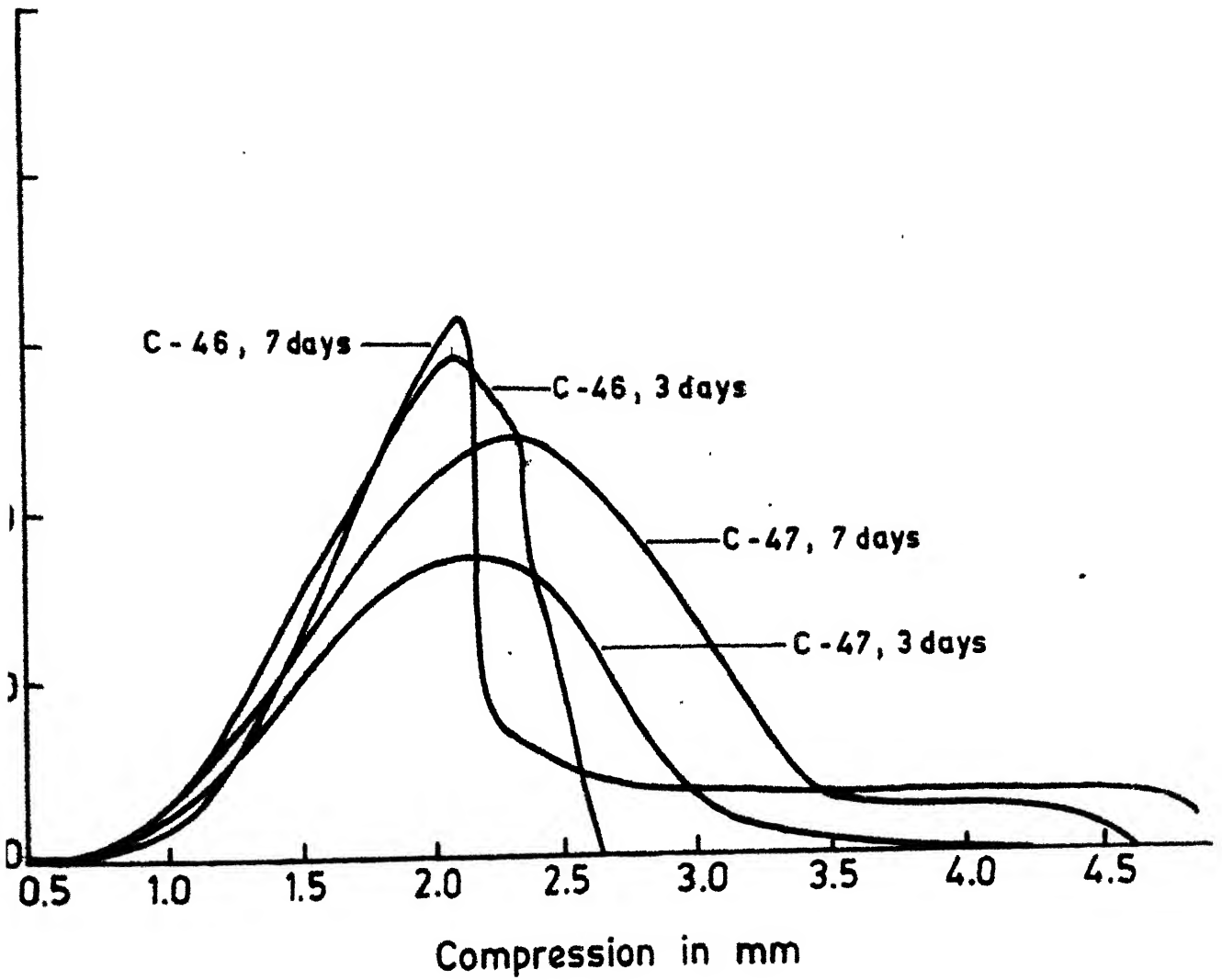
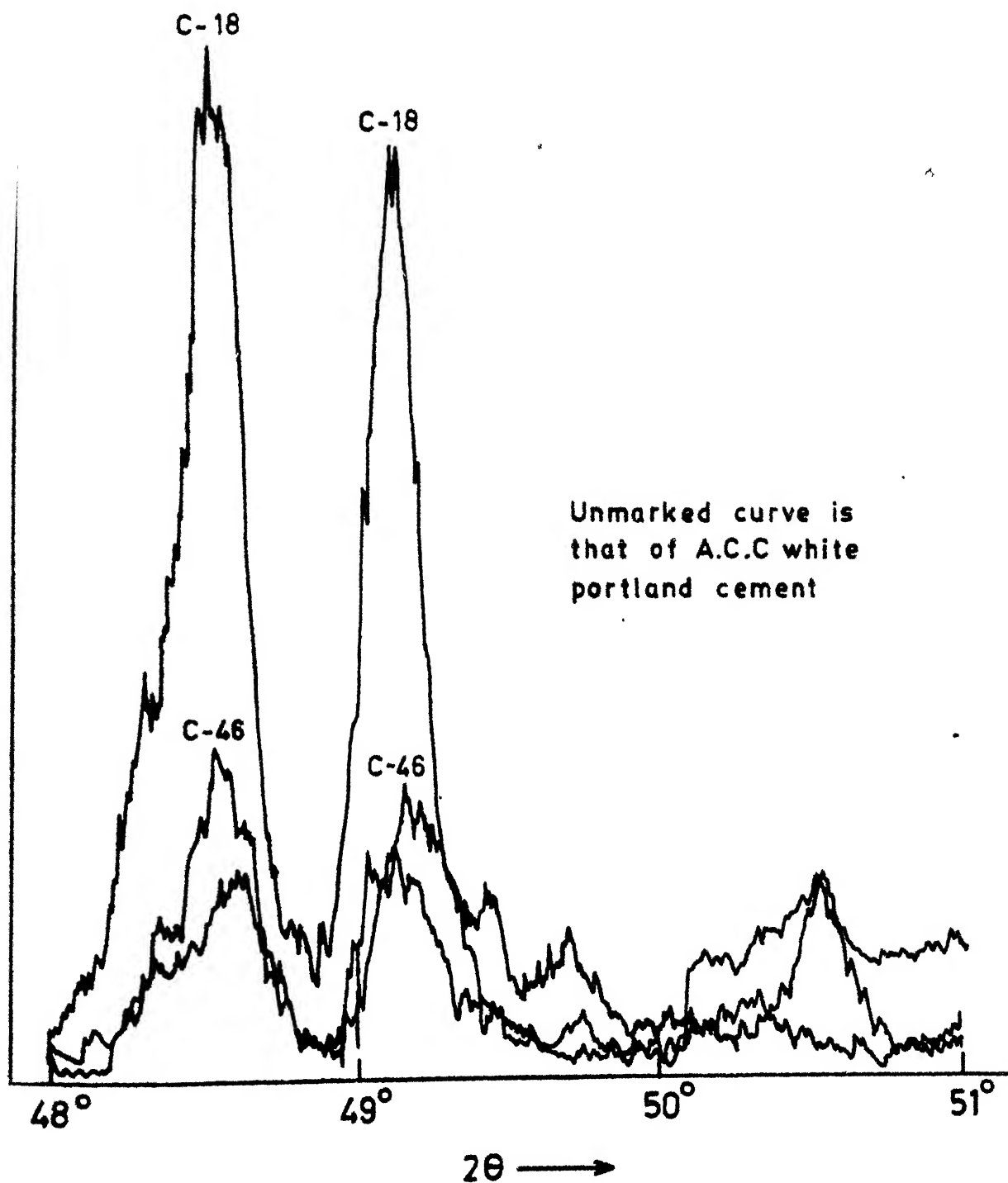g. 6.1 Stress strain plot of cement sand mortar cube.

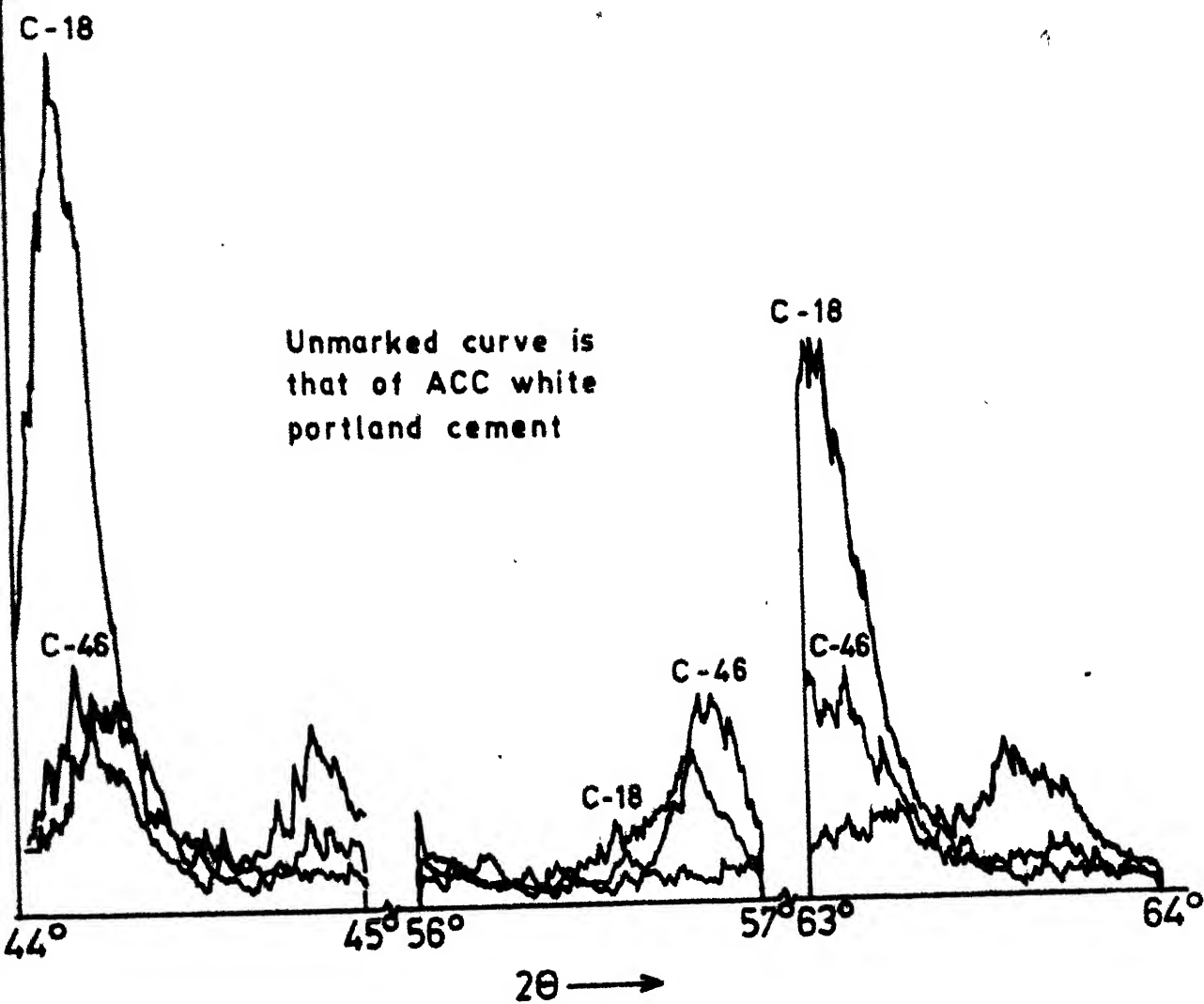Fig.6.2   X-ray diffraction pattern of cement samples.

Fig.6.3   X-ray diffraction pattern of cement samples.

white portland cement. The relative amount of $-C_2S$ is also much lower. Some of this can be verified from Fig. Nos. 6.2 and 6.3 given in page nos. 161 and 162. There is some presence of free CaO, but then it is so less in amount that its presence is insignificant.

Use of 2 wt.% sodium silico-fluoride gives rise to friable clinker with satisfactory workability. The cement tap-density is 0.894 gms./c.c. as compared to 1.16 gms/c.c. for A.C.C. white portland cement. This means each bag of 50 kgs. will contain an excess of 12,825 c.c. of cement. So with 2 wt.% $NaSiF_6$, the consumer gets 29.75% extra cement by volume, without any extra cost.

With 2 wt.% sodium silico-fluoride, the colour is reddish gray and not white. But then this problem is not all that severe because when cured in water, within one day, the colour not only becomes white, but in fact it gets whiter than the A.C.C. white portland cement. The colour of A.C.C. white portland cement does not improve when cured under water.

As far as the heat treatment is concerned, it was found that rapid cooling of clinkers is the best mode of cooling. This was infact essential when 2 wt.% $NaSiF_6$ is used as a flux. With fan cooling the strength is so high that inspite of the extra rapid development of strength in air cooled samples, it cannot catch up with the strength of fan cooled samples within 7-days. Fan cooling gives scope

for the use of heat-recuperators which help in raising the thermal efficiency of the kiln.

From the point of view of temperature, it was found that the strength developed parabolically with rise in the firing temperature. But 1150°C was chosen to be the best temperature for firing, because with just 5 hours of soaking time, it was the lowest temperature at which the strength was found to be higher than the A.C.C. white portland cement at all ages. At 1150°C the colour of the cement was lighter. From reddish gray the colour changed to pinkish white. Besides with lowering of the temperature the tap-density further fell down to 0.669 gms./c.c. This means, with every 50 Kgs. bag, for the same price the customer will get 73.39% extra cement by volume. This has a great significance in making the cement cheaper. Besides a temperature as low as 1150°C implies lower cost of furnace construction, lower expenditure in radiative and convective loses and lower maintainence cost.

From the point of view of the soaking time, 4 hours was found to be most satisfactory at 1150°C. Higher soaking time at 1150°C gave far excess strength than that are required. There was no point in firing at 1100°C with more than 9-hours of soaking time because there was no significant advantage associated with lowering the temperature by 50°C. An increase of soaking time by 5 hours was more expensive an alternative. At 1150°C with 4 hours of soaking time the heat input towards

the production of cement is much lower than that required in the conventional process. This makes this cement much cheaper. Besides with 4 hours of soaking time at 1150°C the clinker is quite friable and the cement workability quite satisfactory. The colour is purplish gray. As already mentioned this colour vanishes after 1 day of water curing.

From the point of view of raw material morphology, white rice husk ash, hydrated lime of commercial grade and activated Bayer's alumina were found best. White rice husk ash means that the carbonaceous material will have to be removed and hence a little cost involved with it will have to be borne. Hydrated lime of commercial grade implies that a very cheap source of lime, like slaked lime coming out of the acetylene plant, can be used with superior effects. Activated Bayer's alumina implies that the excess cost involved with the prolonged activation process will have to be borne. But inspite this restrictions on the whitness of the rice husk ash and the activity of the Bayer's alumina, still the cement production will turn out to be much cheaper than the conventional process. Because rich husk ash is very cheap, and no purification step is required for removing Fe_2O_3, TiO_2, Mn_2O_3 etc. Again lime need not be crushed or ground.

Bulk cement (about 1.5 kgs.) was then made using white rich husk ash, commercial grade hydrated lime, actified Bayer's alumina and 2 wt.% sodium silico-fluride by firing at

1150°C for 4 hours. The result can be seen from Fig. No. 6.1 given in page no. 160 or from the table no. 5.1.4 given in page no. 122. The 3-days and the 7-days strength of cement-sand mortar cubes, containing 1:3 cement/sand ratio and 2:1 cement/water ratio, was found to be 65.57% and 31.28% higher than the corresponding values for A.C.C. white portland cement. The superior strength is justified by the xtra height of the peaks pertaining to the cementing phases, as can be seen from figure numbers 6.2 and 6.3 given in page nos. 161 and 162.

So we conclude by reiterating that cheaper white portland cement of superior quality can be made from rice husk ash, commercial grade hydrated lime, actified Bayer's alumina and 2 wt.% sodium silico-fluoride.

Keeping in view the promise held by this process, for the white portland cement production, the following suggestions are being offered for the future work.

1. One should try and remove the colour associated with the use of sodium silico- fluoride as a flux. One can either study the mechanism of the colour formation with the idea of finding out whether this mechanism can be halted without affecting the fluxing action. The other option would be to try and mask the colour with the help of optical whitners.

2. Attempts should be made towards making white portland cement using dried coconut shells as a source of silica.

Use of such recurring raw materials, which otherwise
lead to environmental pollution,needs attention.

3. The idea of making ordinary portland cement from rice
husk ash should not be lost sight off. A mixture of
rice husk ash, hydrated lime, Bayer's alumina, iron
oxide, sodium silico-fluoride and powdered coal could
generate cheap ordinary portland cement through a
lower-energy route.

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